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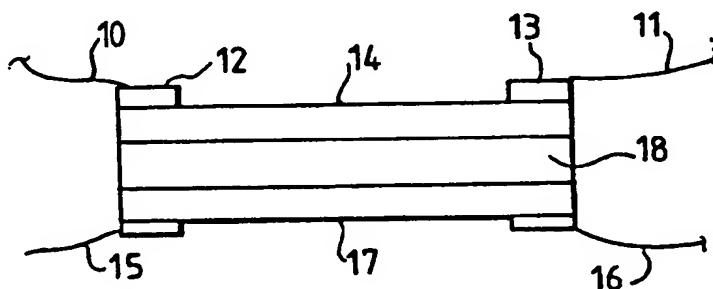
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(71) Applicant (for all designated States except US): CAPTEUR SENSORS & ANALYSERS LTD. [GB/GB]; 66 Milton Park, Abingdon OX14 4RY (GB).		Published With international search report.	
(72) Inventors; and (75) Inventors/Applicants (for US only): McGEEHIN, Peter [GB/GB]; School Road, Compton RG 0QU (GB). MOSELEY, Patrick, Timothy [GB/GB]; Ivy Cottage, South Row, Chilton, Didcot OX11 0RT (GB). WILLIAMS, David, Edward [GB/GB]; 41 Oxford Road, Abingdon OX14 2EE (GB). HENSHAW, Geoffrey, Stephen [NZ/GB]; 38 Rossiter Road, London SW12 9RU (GB). DAWSON, Darryl, Hirst [GB/GB]; 13 Farnborough Avenue, London E17 6HX (GB). GELLMAN, Laura, Jane [GB/GB]; 173 Canterbury Road, Harrow HA1 4PA (GB).			

(54) Title: SEMICONDUCTING OXIDE GAS SENSORS AND MATERIALS THEREFOR

(57) Abstract

The selectivity of response of resistive gas sensors to specific gases or vapours is improved by the selection of specified gas-sensitive materials which are not previously known for the applications described, which include detection of hydrocarbons in the presence of CO, H<sub>2</sub>S, SO<sub>2</sub>, chlorine, NO<sub>2</sub>, CO<sub>2</sub> (especially in low concentrations), CFC's, ammonia, free oxygen by determination of partial pressure, and numerous organic gases and vapours.



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**SEMICONDUCTING OXIDE GAS SENSORS AND MATERIALS THEREFOR**

This invention relates to resistive gas sensors;  
methods of making such sensors; sensor arrays  
comprising such sensors; and methods of using such  
5 sensors and arrays.

Such a sensor, as is well known, comprises, in general  
terms, a semiconducting sensing element such that its  
electrical resistance changes, in response to a change  
10 in the concentration of at least one gas or vapour  
(sometimes referred to as a "target gas") that is  
present, to a substantially greater extent than to other  
gases or vapours.

The sensor is thus selective in favour of the target gas  
and is accordingly used for detection, and, where  
15 required, measurement, of the target gas.

Such a sensor will be referred to as a sensor of the  
kind specified.

Semiconducting oxide materials, when used for gas  
sensors, provide devices which are inexpensive, light  
20 and robust. However, they suffer a reputation for  
unacceptable cross-sensitivity to different gases,  
particularly to water vapour, which is always present in  
the atmosphere at concentrations which can vary widely.  
Devices based on tin dioxide, such as are widely used,  
25 show strong effects of changes in relative humidity,  
both on the baseline resistance and on the sensitivity  
of the resistance change to the presence of gases such  
as carbon monoxide.

These devices also have a reputation for excessive

baseline drift and show a long stabilisation time in the atmosphere after the temperature of the device has first been raised to its operating value. The present invention aims to provide sensor materials which are  
5 more selective than those in current use, particularly in respect of the discrimination of changes in the concentration of the gas to be detected from the effects of varying relative humidity.

A second object of the invention is to provide sensor  
10 materials with short stabilisation time and greatly reduced baseline drift in comparison with those devices that are currently in common use.

A third object of the present invention is to provide  
15 sensor materials which offer improved selectivity and sensitivity for certain gases whose detection in the environment is of concern, including sensor materials useful for the measurement of oxygen partial pressure, for example in breathing atmospheres or in the exhaust gases of combustion, and sensor materials useful for the  
20 measurement of reactive gases such as hydrogen sulphide in anaerobic atmospheres.

A fourth object is to provide certain combinations of sensors utilising different materials which can then be used, in various ways well known in the art, to provide  
25 more reliable alarm indications for certain conditions that might be injurious to health and safety.

It has been suggested (in the paper by D. E. Williams and P. T. Moseley, J Materials Chemistry, 1 (1991) 809-814) that the behaviour of semiconducting oxide  
30 materials can be manipulated by manipulation of the crystallite size and surface area per unit mass of the

material exposed to the gas, and of the concentration of electrically active donor species present in the lattice, so as to give changes characteristic either of n-type materials (resistance decreases in reducing gases and increases in oxidising gases); or of p-type materials (resistance increases in reducing gases and decreases in oxidising gases); or of mixed behaviour.

The same paper also suggested that, by a fortuitous combination of the concentration of electrically active donors and the surface area per unit mass, some selectivity to certain gases might be obtained.

In the light of these disclosures, it is possible to try substituting elements of different valency into some parent composition, and to try making variations in the preparation of materials so as to obtain different surface areas per unit mass, in an attempt to achieve a degree of selectivity. However, the above paper offers no prescription for the choice of suitable parent compositions, and implies that wide selectivity might require specific interaction of the target gas with the surface, as well as tuning of the composition and surface area. The paper therefore leads to a conclusion that the observation of a wide selectivity of response in a semiconducting oxide material would be rather surprising; and that, furthermore, it would be very surprising indeed to find a high degree of selectivity of response where no specific interaction with the surface were anticipated - for example, a high selectivity of response for hydrocarbons over carbon monoxide.

The above mentioned paper is silent on the question of

discrimination of the effects of the desired target gas from the effects of variation in relative humidity. It will also be appreciated, especially from the study of the art of catalysis, that substitutions of different elements into a lattice can serve to vary the surface density and nature of the gas adsorption sites present on the surface of the material. Such sites are often classified as acidic or basic, according to whether they can interact with gases such as ammonia on the one hand or hydrogen sulphide or carbon dioxide on the other. For example, it is often said that the substitution of chromium into a lattice serves to increase the acidity of the surface sites. However, it is by no means clear how such adsorption sites couple into the charge carriers present in the solid, so that a change in the adsorption of dissociation of a gas molecule on such a site could give rise to a change in the measured conductivity of the solid material.

The present invention proposes some materials for use in gas sensors, having improved selectivity of response to different gases. Specific examples are as follows.

1.  $\text{Ba}_6\text{Fe}_{(1+x)}\text{Nb}_{(9-x)}\text{O}_{30}$ , in which  $2.1 > x \geq 0$ , and in which, preferably,  $0.8 > x \geq 0.01$ . This composition range shows a strong selectivity of response for hydrocarbons over carbon monoxide, being a selection from the range disclosed in patent specification GB 2 149 122; this composition range is such that the material has a tetragonal tungsten bronze structure. In this system, the selectivity can be adjusted by alteration of the microstructure, which can conveniently be done by adjustment of the sintering temperature.

Further possible variations, again selected from the disclosure of the document GB-A-2 149 122, show the same basic crystal structure, while exhibiting useful properties of selectivity. These variations have the additional advantage that, not containing barium, they are less susceptible to decomposition under the influence of acidic gases such as sulphur dioxide, which might be present in the atmosphere under test. One example is  $A_2B_4Fe(3+x)Nb(7-x)O_{30}$ , where: A is a divalent element of large ionic size, such as Pb; B is a trivalent element such as neodymium (Nd); and  $3.1 \geq x \geq 0$ .

Another example is  $A_6B_4Fe(4+x)Nb(6-x)O_{30}$ , in which: A is a trivalent element of large ion size, such as Bi; B is also a trivalent element such as Nd or Bi; and  $4.1 \geq x \geq 0$ .

2.  $Cr(2-x)Ti_xO_3$ , in which  $0.3 \geq x \geq 0.1$ , being a selection from the composition range disclosed in the document GB-A-2 202 948, which shows a strong response to ammonia and hydrogen sulphide. This range of materials is also useful for the measurement of volatile alcohols, aldehydes, including dialdehydes such as glutaraldehyde, ketones, such as butan-2-one, hydrocarbons other than methane, including gasoline, ethers, including diethers such as dimethoxyethane, and sulphur dioxide. It is useful for the measurement of hydrogen sulphide in anaerobic atmospheres, as in the measurement of concentrations of hydrogen sulphide in carbon dioxide. It shows particularly good baseline stability and discrimination against the effects of varying relative humidity.

3.  $Ti(1-x)Cr_xO(2+y)$ , in which  $0.2 \geq x > 0$  and y is variable

according to the temperature and oxygen partial pressure, being a composition useful for the measurement of oxygen partial pressure, having a temperature sensitivity of conductance which is significantly less than that of  $\text{TiO}_2$  and being resistant to poisoning by acid vapours such as  $\text{SO}_2$ .

4.  $\text{Fe}(1+x-z)\text{A}_z\text{Nb}(1-x)\text{O}_4$ , in which A is either a pentavalent element (such as Nb itself or Ta), or a hexavalent element such as W, with  $0.1 \geq x \geq 0$  and  $0.1 \geq z \geq 0$  in both cases; and  $\text{Fe}(1-x)\text{B}_x\text{NbO}_4$ , in which B is either a trivalent element such as Al or Cr, with  $1 \geq x \geq 0$ , or a tetravalent element such as Zr or Ti, in which case  $0.1 \geq x \geq 0$ .

This range of compositions is particularly useful in the measurement of oxidising gases such as chlorine, nitrogen dioxide and ozone. These compounds show useful selectivity over interfering gases such as carbon monoxide and hydrocarbons. Their composition ranges are a selection and extension of the range disclosed in the document GB-A-2 149 120. These compositions are also useful for the measurement of small concentrations in the atmosphere of aldehydes, ketones, ethers, including diethers, and esters, including unsaturated esters such as methyl methacrylate.

It will be appreciated that the purpose of the substitutions of elements A and B into the iron niobate lattice is to manipulate the concentration of charge carriers in the lattice, which are present by virtue of the properties of variable valency of both Fe and Nb, and also to manipulate the number and nature of gas adsorption sites present at the surface of the material.



The first range is essentially a substitution of Nb, and the second is one of Fe.

It will also be appreciated that combinations of substitutions of both iron and niobium are equally feasible, and that elements other than those cited above may also be substituted into the lattice, provided that their ionic size is not such as to cause a disruption of the lattice structure.

5.  $(\text{Fe}_{1-x}\text{Cr}_x\text{NbO}_4)_a(\text{B}_{1-y}\text{A}_y\text{O}_2)_{(1-a)}$ , in which  $1 \geq a \geq 0$ ,  $1 > x > 0.1$ ,  $0.1 > y > 0$ , B is Ti or Sn, and A is an element of valency greater than 4 (for example A might be Nb, Ta, W or Sb), being a solid solution series of compositions having the rutile crystal structure. It will be appreciated that, in this case, the variation of the ratio Fe/Cr (the number x) serves to vary the acidity of the surface sites provided by Fe and by the element B, while variation of the ratio a serves to change the relative number of the sites provided by element B. Variation of the ratio B/A (the number y) serves to vary the concentration of electrically active donor states in the lattice. The electrically active donor states can be provided by partial reduction of the element B in order to compensate for the excess valency of element A. This range of materials provides compositions useful for the detection of low concentrations of carbon monoxide, at relatively low operating temperature.

6.  $\text{BaSn}_{1-x}\text{Sb}_x\text{O}_3$ , in which  $0 < x < 0.1$ , being an extension of a range of materials disclosed in GB-A-2 149 121, having an electrical conductivity usefully increased above that of the parent composition  $\text{BaSnO}_3$ , and having electrical conductivity at temperatures above  $300^\circ\text{C}$

surprisingly sensitive to the presence of small concentrations of carbon dioxide in the air. This conductivity change is specific to the presence of carbon dioxide, and is not an effect of changes in the oxygen partial pressure contingent upon the introduction of carbon dioxide.

Sensors fabricated from this material are useful in the monitoring of atmospheres in buildings, particularly air-conditioned buildings which suffer from the so-called 'sick building syndrome'; in the monitoring of breathing atmospheres such as in closed-circuit breathing apparatus; and in the monitoring of atmospheres in areas in which carbonated beverages are handled in bulk.

7.  $\text{Sr}_{(1-b)}\text{Ba}_b\text{Fe}_{(1-y)}\text{A}_y\text{O}_{(3-x)}$ , where  $1 \geq b \geq 0$ ,  $x$  is a variable determining the degree of oxygen deficiency of the lattice, being dependent on the temperature and oxygen partial pressure and generally falling within the range  $0.5 \geq x \geq 0$ , and  $A$  represents an element with valency 6 or more (e.g.  $A$  is tungsten, molybdenum or uranium) replacing a part (represented by  $y$ ) of the iron in the ferrate lattice. This composition is useful for the measurement of variations in oxygen partial pressure.

8.  $\text{WO}_3$ , prepared in the form of a porous thick film, which is extremely and surprisingly sensitive to small concentrations of chlorine and nitrogen dioxide in air, giving extremely good discrimination against the effects of varying relative humidity, and against the effects of hydrocarbons and carbon monoxide which might also be present in the atmosphere.

In a first aspect, the invention provides a gas sensor

of the kind specified, in which the sensing element material is selected as set forth in the characterising part of Claim 1, according to the selection of target gases also set forth therein.

- 5 In other aspects, the invention provides sensor arrays, methods of making sensor elements, and methods of detecting at least one target gas, as set forth in the other claims hereof.

Various embodiments of the invention will now be  
10 discussed, with reference where appropriate to known prior art. This description, for convenience, is divided into headed sections, in which the use of different sensing element materials (referred to for short as "sensor materials") for specific purposes are  
15 discussed.

A number of non-limiting examples will be given, and reference will be made to the accompanying drawings, in which:-

Figure 1 is a diagram comparing the response curve of a  
20 first barium iron niobate sensor material to the presence of CO in a gas mixture with that of propane in a gas mixture;

Figure 2 is a similar diagram for another barium iron niobate sensor material in propane;

25 Figure 3 is equivalent to Figure 1 but is expressed in different terms to show straight-line responses;

Figure 4 is a histogram comparing response coefficients (as defined below) for different barium iron niobates in propane and CO;

Figure 5 is a diagram showing variation with time of the resistance of a sensor device composed of  $\text{Cr}_{1.8}\text{Ti}_{0.2}\text{O}_{(3+x)}$  before being pretreated, when exposed to various small concentrations of  $\text{H}_2\text{S}$  in air;

- 5     Figure 6 is similar to Figure 5 for the same device after pretreatment;

- Figure 7 consists of a resistance-gas concentration diagram for a similar pretreated device in  $\text{H}_2\text{S}$ , and, below it, a similar diagram for the ratio  
10      $(R_{\text{gas}} - R_{\text{air}})/R_{\text{air}}$ ;

Figure 8 shows an X-ray photoelectron spectrum for a chromium-titanium oxide specimen, partially pretreated;

Figure 9 is similar to Figure 8 for the same specimen when fully pretreated;

- 15     Figures 10 and 11 show the response to CO of a chromium-titanium oxide sensor, in terms of resistance plotted against a function of CO concentration for various values of humidity, at two different temperatures;

- Figure 12 is a resistance/time diagram for a chromium-niobium oxide sensor, showing its response to various  
20     concentrations of CO in air;

- Figure 13 is a response diagram showing variation in the resistance of a barium-tin-antimony oxide sensor with time, in response to various concentrations of CO in  
25     air;

Figures 14 to 17 are similar response diagrams for a  $\text{WO}_3$  sensor, showing its response to various different gases; and

Figures 18 and 19 are similar response diagrams for a barium-tungsten-iron oxide sensor in response to the partial pressure of oxygen in a gas mixture.

**Sensor material discriminating between hydrocarbons and carbon monoxide**

Hydrocarbons and carbon monoxide occur together in the exhaust gas from combustion. In some applications, it is necessary to measure the hydrocarbon content of the gas stream, without interference from carbon monoxide: a particular example is in the monitoring of the efficiency of a 3-way catalyst fitted to a motor vehicle. Since hydrocarbons are the main source of smog, confirmation that their concentration has been diminished to a suitably low level is required.

Semiconducting oxide, gas-sensitive resistors are attractive devices to consider for this application because they are inexpensive, robust and sensitive. A difficulty with devices in common use (e.g. devices based upon tin dioxide) is that the signal due to carbon monoxide is often as large as, or larger than, that due to hydrocarbons.

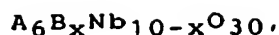
It is an object of the present invention to provide materials having much greater sensitivity to hydrocarbons (propane, butane, pentane, hexane, heptane and octane) than to carbon monoxide.

The above mentioned document GB-A-2 149 122 discloses a sensor which is suitable for use in a gas or gaseous mixture, and which includes a gas-sensitive material having an electrical characteristic which is variable in response to the presence of a gas. This material contains, or consists of, a complex oxide of niobium, and has either the general formula:



where:  $A, B = Pb, Ba \text{ or } Sr$ , and  $1 > x \geq 0$ , or the general

formula:



where: A is divalent (e.g. Sr, Ba or Pb) or trivalent (e.g. Bi) or tetravalent (e.g. Zr and Ce); and A may be partially substituted by a monovalent element such as K, Na, Li or Cu. The value of x depends upon the valencies of B and A, and is in the range  $4 > x \geq 0$ . B may be chosen from divalent transition metals (e.g. Co, Ni and Mn), or trivalent elements (e.g. Fe), or tetravalent elements (e.g. Ti). B can be an element capable of exhibiting a variable valency in the solid. One of the compounds mentioned was  $Ba_6FeNb_9O_{30}$ .

We have found that a selection can be made, in this range, of a group of materials which show a strong selectivity of response for propane and higher hydrocarbons over carbon monoxide.

Their compositions are  $Ba_6Fe(1+x)Nb(9-x)O_{30}$ , in which  $2.1 > x \geq 0$ , and in which, preferably,  $0.8 > x > 0.01$ . Powder diffractometry has shown that the compositions were tetragonal tungsten bronzes.

The invention also provides sensors for the measurement of oxygen partial pressure, particularly, but not exclusively, in the exhaust gases of spark ignition internal combustion engines supplied with lean fuel/air mixtures, that is mixtures in which the fuel:air ratio is less than the stoichiometric combustion ratio of approximately 1:14 by weight.

It has previously been proposed in the document US-A-4 454 494 to provide an oxygen sensor comprising a

ferrate of strontium, barium, or strontium/barium, and wherein the iron in the ferrate lattice has been replaced by an element of valency greater than 3. Examples of such an element valency greater than 3 are  
5 given as titanium, cerium, tantalum and niobium. We have now been surprised to find that the use of elements exhibiting valencies of 6 or more, as replacement for part of the iron in the ferrate lattice of strontium, barium or strontium/barium ferrate oxygen sensor, gives  
10 significantly improved results in respect of signal stability under DC interrogation, i.e. when the sensor is excited by a unidirectional voltage.

Thus, in an embodiment of the invention, an oxygen sensor exhibiting a change in electrical resistance as a  
15 function of oxygen partial pressure comprises at least one of strontium ferrate ( $\text{SrFeO}_{3-x}$ ), barium ferrate ( $\text{BaFeO}_{3-x}$ ), and strontium barium ferrate ( $\text{Sr}_{1-b}\text{Ba}_b\text{FeO}_{3-x}$ ), where  $x$  is a variable and determines the degree of oxygen deficiency of the oxide. The value  
20 of  $x$  depends upon temperature and oxygen partial pressure, but it generally falls within the range 0-0.5. The value of  $b$  is 0-1, with part of the iron in the ferrate lattice having been replaced by at least one element selected from the group exhibiting valencies of  
25 6 or more.

Referring now to Figures 1 to 4, Figure 1 shows the dependence of resistivity on gas concentration for the composition  $\text{Ba}_6\text{Fe}_{1.4}\text{Nb}_{8.6}\text{O}_{30}$  at  $470^\circ\text{C}$ , giving a  
30 comparison between the response to propane ( $\text{C}_3\text{H}_8$ ) and the response to carbon monoxide.

Figure 2 shows the propane response of the resistivity



of the compound  $\text{Ba}_6\text{Fe}_{1.6}\text{Nb}_{8.4}\text{O}_{30}$ , at  $500^\circ\text{C}$ , and demonstrates that the response is very strong at low concentrations of propane.

5 Figure 3 shows the response of  $\text{Ba}_6\text{Fe}_{1.4}\text{Nb}_{8.6}\text{O}_{30}$  to both propane and CO at  $470^\circ\text{C}$ , expressed as the ratio of the change in conductivity in the presence of the gas concerned to its conductivity in air, and which may be calculated as the ratio  $(R_{\text{air}} - R_{\text{gas}})/R_{\text{gas}}$ . This response varies as the square root of the gas concentration.

10 Figure 4 shows the slope of graphs as in Figure 3 for the compositions studied, i.e.  $\text{Ba}_6\text{Fe}_{(1-x)}\text{Nb}_{(9-x)}\text{O}_{30}$ , with the values of x being given on the horizontal axis. Figure 4 compares the behaviour of these compositions in response to propane (P) with that in response to carbon  
15 monoxide (C).

The slope of the graph of Figure 3 is a measure, independent of concentration, of sensitivity to a particular gas, and is termed here the response coefficient. Other measures could be used which would  
20 equally confirm the enhanced response to propane over that to carbon monoxide, for example the resistance change in response to some arbitrarily chosen concentration. Figure 4 shows that, at a concentration of 150 ppm, the change in resistance in response to  
25 propane is about seven times that in response to carbon monoxide.

The slope of the graph of Figure 3 is a concentration-independent measure of the sensitivity to a particular gas, and is termed here the response coefficient. Other  
30 measures could be used which would equally confirm the enhanced response to propane over that to carbon

monoxide: for example, the resistance change in response to some arbitrarily chosen concentration; Figure 4 shows that, at a concentration of 150ppm, the change in resistance in response to propane is about seven times that in response to carbon monoxide. For this material, the selectivity of response to propane over carbon monoxide varied according to the microstructure, which depended in turn upon the sintering temperature employed to fabricate the material into a gas-sensitive element. If the material was oversintered then the porosity was low, and both the sensitivity and selectivity were poor. If the material was under-sintered, then the grain size was too small, the sensitivity was large but the selectivity was poor.

An important parameter determining the usefulness of a material as a gas sensor is the magnitude of the response to changes in relative humidity, in comparison with the response to changes in gas concentration. Table 1, below, shows results for the composition  $\text{BaFe}_{1.6}\text{Nb}_{8.4}\text{O}_{30}$ . It demonstrates that the response to propane, and to other hydrocarbons introduced into the gas stream by injection of a small aliquot of liquid, so as to give an unknown but small gas concentration, is much larger than the resistance change caused by changing the atmosphere from dry air to air at 100% relative humidity at room temperature.

Table 1: Response of  $\text{BaFe}_{1.6}\text{Nb}_{8.4}\text{O}_{30}$ 

<u>Gas composition</u>	<u>resistance</u>
Dry air	8.6 Mohm
Wet air (100% r.h. at 20°C)	3.2 Mohm
5 Pentane (25 $\mu\text{l}$ injection into dry air)	64 kohm
Hexane (25 $\mu\text{l}$ injection into dry air)	45 kohm
Heptane (25 $\mu\text{l}$ injection into dry air)	38 kohm

10 **Chromium titanium oxide sensors for Hydrogen Sulphide, for use in both aerobic and anaerobic environments**

The document GB-A-2 202 948 discloses compositions of general formula  $\text{Cr}_2\text{Ti}_{(2-x)}\text{O}_{(7-2x)}$ , where  $2 > x > 0$ , claiming these as selective ammonia sensors. The document states that sensors in accordance with that invention may be

15 such that they do not suffer significant interference from other reducing gases commonly encountered (e.g.  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ). The examples given are  $\text{TiO}_2$  - 48.7 mol%  $\text{Cr}_2\text{O}_3(\text{Ti}_{0.51}\text{Cr}_{0.97}\text{O}_{(2-x)})$  and  $\text{TiO}_2$  - 90 mol%  $\text{Cr}_2\text{O}_3(\text{Cr}_{1.8}\text{Ti}_{0.1}\text{O}_{(3+x)})$ . "Techniques and Mechanisms in

20 Gas Sensing", ed. P. T. Moseley, J. O. W. Norrois and D. E. Williams, p.136, and Moseley and Williams, Sensors and Actuators B 1 (1990) 113.5, disclose  $\text{Ti}_{0.9}\text{Cr}_{0.1}\text{O}_{(2-x)}$  as an unselective material, and  $\text{Cr}_{1.8}\text{Ti}_{0.2}\text{O}_3$  as a material selective to ammonia.

25 Surprisingly, we have now found that chromium titanium oxides can be formed into sensor elements which are extremely sensitive to hydrogen sulphide.

We have also found, again to our surprise, that the

response of  $\text{Cr}_{1.8}\text{Ti}_{0.2}\text{O}_{3+x}$  to  $\text{H}_2\text{S}$  is greatly enhanced, in both amplitude and speed of response, by prior treatment of the sensor in an atmosphere containing  $\text{H}_2\text{S}$ : an example of such a pretreatment is exposure for a time of a few minutes (between 1 and 10 minutes) to a concentration of 10 ppm of the gas, at a sensor temperature of greater than about  $200^\circ\text{C}$  and less than about  $600^\circ\text{C}$ . Longer times of exposure, and higher gas concentrations, may be used, but do not give any further enhancement of performance. Sensors prepared in this way have the particular advantage that the interference caused by changes in relative humidity is very small in comparison with the response to hydrogen sulphide: the effect of a change in relative humidity from 0 to 100% at room temperature is equivalent to the response to 10.3 ppm of  $\text{H}_2\text{S}$  when the sensor is operated at  $400^\circ\text{C}$ . When the pretreated sensor is operated at  $250^\circ\text{C}$ , relative sensitivity to  $\text{H}_2\text{S}$  is even higher.

This pretreatment (or preconditioning) leads to a modification of the surface of the material, which can be detected either by photoelectron spectroscopy, or other such surface analytical method, or, conveniently, by temperature programmed desorption. In the latter method, the device is heated in a vacuum and the gases desorbed are detected, for example using a mass spectrometer.

The effect of the pretreatment appears to be permanent at the operating temperature for  $\text{H}_2\text{S}$  detection, and is characterised by an increase of the baseline from that of the virgin material, and a dramatic increase in the sensitivity and speed of response. Temperature-programmed vacuum-desorption studies of the treated

materials showed a loss of  $\text{SO}_2$  from the surface, at temperatures above  $630^\circ\text{C}$ .

5 The  $\text{H}_2\text{S}$  pretreatment of  $\text{Cr}_{1.8}\text{Ti}_{0.2}\text{O}_3$  has been studied by x-ray photo-electron spectroscopy (XPS). As the pretreatment progressed, the S 2p region of the spectra changed. Initially, three peaks were observed: two major peaks at binding energies of 159.0 eV and 164.4 eV, tentatively assigned to sulphide and elemental sulphur species, respectively, and a minor peak at 168.5 eV, attributed to sulphate groups formed on the surface. 10 When the pretreatment was complete, as judged by the effects on the gas response, only a single peak at 168.7 eV was present.

15 The sensor material was prepared by reacting mixed powders of  $\text{Cr}_2\text{O}_3$  and  $\text{TiO}_2$  at  $800^\circ\text{C}$ . A sensor was prepared by depositing, by standard thick-film ceramic fabrication methods, a porous layer of the sensor material over an inter-digitated pattern of gold electrodes supported on an alumina substrate. On the 20 reverse side of the substrate was printed a platinum track. The device was heated by applying a current to the platinum track using a Wheatstone bridge arrangement to keep the platinum track at constant resistance and hence constant temperature.

25 Figure 5 shows the resistance-time variation of a sensor device of composition  $\text{Cr}_{1.8}\text{Ti}_{0.2}\text{O}_3$ , upon initial exposure to small concentrations of  $\text{H}_2\text{S}$  in air, at an operating temperature of  $370^\circ\text{C}$ . The baseline shift caused by the first exposure is clear.

30 Figure 6 shows subsequent gas exposures. In contrast to the first exposure, the response to 5ppm gas is now

rapid and substantial. In both Figures 5 and 6, the left hand scale and the line without symbols show the temperature (370°C). "50% moist" means a relative humidity of 50% in clean air.

5 Figure 7 shows the gas response law for a pretreated similar sensor, at 370°C, illustrating the dependence on the square root of the concentration. In the lower diagram of Figure 7, the ratio of ( $R_{\text{gas}} - R_{\text{air}}$ ) to  $R_{\text{air}}$  shows a straight line relationship when plotted against  
10 the square root of gas concentration, where  $R_{\text{gas}}$  and  $R_{\text{air}}$  are the resistance in the gas and in air, respectively.

The response, at temperatures appropriate to the detection of hydrogen sulphide ( $\leq 400^\circ\text{C}$ ), of the  
15 pretreated sensor to methane, hydrogen, hydrocarbons and carbon monoxide, present in the air, was very small, so that these sensors are very useful for the detection of hydrogen sulphide in a background of such gases. Circumstances where such selectivity is of importance  
20 include monitoring for hydrogen sulphide around a natural gas installation.

Pretreatment can be detected by x-ray photoelectron spectroscopy (XPS) of the sensor surface. Figure 8 shows an XPS spectrum of a partially treated specimen  
25 (exposure to 1ppm  $\text{H}_2\text{S}$  at  $200^\circ\text{C}$ ). It should be noted that, because of an instrument effect, the binding energy scale on this diagram has to be increased by 3.6eV. Figure 9 shows an XPS spectrum of a completely treated specimen (50ppm exposure at  $200^\circ\text{C}$ ). The binding  
30 energy scale on this diagram is too low by 3eV.

The literature on the behaviour of semiconducting oxides

as sensors for reactive gases universally and unambiguously states that such detection requires the presence of oxygen, preferably at levels such as are found in the air. We have now found that chromium  
5 titanium oxides can be used to measure low concentrations of hydrogen sulphide in an anaerobic or substantially anaerobic environment, such as pure carbon dioxide. In this case, also, pretreatment with hydrogen sulphide enhanced the response. Such sensors are useful  
10 in the control of processes such as anaerobic fermentations.

The response of a sensor, pretreated as above, to hydrogen sulphide in carbon dioxide is as follows:

Composition:	$\text{Cr}_{1.8}\text{Ti}_{0.2}\text{O}_3$
15 Operating temperature:	400°C
Resistance in pure $\text{CO}_2$ :	80kohm
Resistance in pure $\text{CO}_2$ containing 500ppm $\text{H}_2\text{S}$ :	770kohm

20 Chromium titanium oxide sensors for hydrocarbons and carbon monoxide, with improved baseline stability and rejection of effects of varying relative humidity

Tin dioxide and compositions derived from and largely comprising tin dioxide are widely cited in the art and  
25 are used in gas sensitive resistors. However, devices fabricated from tin dioxide show a very large baseline drift upon being heated to the operating temperature: a change of more than 100% over a period of 12 hours is not uncommon. Furthermore, this drift can continue for  
30 a period of weeks or even months, necessitating constant

checking and recalibration. The baseline resistance of tin dioxide devices is also very sensitive to changes in relative humidity: typically, the resistance will halve if the atmosphere is changed from one which is dry  
5 (<2%RH) to one which wet (>70%RH). The sensitivity to carbon monoxide is also greatly affected by changes in the ambient relative humidity.

Although the previous literature implies that compositions of chromium titanium oxide which are  
10 chromium-rich should be insensitive to hydrocarbons and carbon monoxide, we have now been surprised to find that sensors prepared from these materials, as described herein, can be operated at a temperature such that the response, at concentrations of importance for health and  
15 safety monitoring, to propane (operating temperature 475°C), and to carbon monoxide (operating temperature 320°C - 390°C) is substantially greater than the interference caused by a change of relative humidity between 0 and 100% at room temperature.

20 In contrast to the behaviour exhibited by tin dioxide, sensors fabricated from these materials reach a stable resistance within five minutes of being energised, and show a subsequent baseline drift of less than 0.5% per month. These materials therefore form sensors of great  
25 utility for carbon monoxide and hydrocarbons other than methane. The responses to methane and hydrogen are very small, so the sensors are very useful for the detection of carbon monoxide in the presence of a background of methane and/or hydrogen. Circumstances where such a  
30 selectivity is of importance include monitoring for carbon monoxide in a coal mine, or in the monitoring for leakage for carbon monoxide from domestic gas-fired



appliances.

Figures 10 and 11 show the response of a  $\text{Cr}_{1.8}\text{Ti}_{0.2}\text{O}_3$  sensor to various concentrations of carbon monoxide in the air, at various temperatures and relative humidities (referred to an ambient atmosphere at  $20^\circ\text{C}$ ), and at  $415^\circ\text{C}$  in Figure 10 and at  $370^\circ\text{C}$  in Figure 11. The response is larger at lower temperature, but if the temperature is too low, then an effect of variation of relative humidity on the sensitivity to CO becomes apparent. The chosen operating temperature of  $390^\circ\text{C}$  represents a satisfactory compromise in which the response is adequately large and the effect of relative humidity changes rather small.

In general, the material shows a resistance increase in response to the presence of reducing gases in the atmosphere, and the ratio of resistance in the presence of the gas to resistance in the absence of the gas increases with the square root of the gas concentration.

Exposure to hydrogen sulphide at temperatures between  $150^\circ\text{C}$  and  $400^\circ\text{C}$  has the effect of considerably diminishing the response to carbon monoxide, and to other gases for which the operating temperature is below approximately  $450^\circ\text{C}$ .

Table 2 shows that a range of compositions in the series  $\text{Cr}_{(2-x)}\text{Ti}_x\text{O}_3$  is sensitive to carbon monoxide, and has the characteristic that the effect of a change in relative humidity from zero to 100% gives a signal equivalent to only a small concentration of carbon monoxide (the number is given as the 'figure of merit' in Table 2).

Table 2: Response to 300ppm carbon monoxide in the air (50% relative humidity at 20°C) of sensors fabricated from a range of compositions in the series  $\text{Cr}_{(2-x)}\text{Ti}_x\text{O}_3$

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x	(Resistance in presence of CO)/(Resistance in the absence of CO)	Figure of merit (ppm CO equivalent of change in relative humidity from zero to 100%)
0.05	2.6	0.67
0.10	4.3	0.66
0.15	4.3	0.5

### Chromium titanium oxide sensors for sulphur dioxide

Although many sensor materials show resistance response to the presence of sulphur dioxide, the problem with measurement of this gas using this technology is that  
5 the sensors often rapidly become poisoned. Sometimes this is due to the formation of metal sulphates which are molten at the operating temperature. Sometimes it is because of an irreversible adsorption of the gas.

10 It is not obvious how to choose a material which gives a satisfactory response to  $\text{SO}_2$ , which is small in comparison with the effects of change in relative humidity, and which also is not poisoned by the presence of the gas and shows a reversible response. Table 5  
15 shows that a sensor made from  $\text{Cr}_{1.8}\text{Ti}_{0.2}\text{O}_3$  shows a satisfactory response in comparison with the effects of changes in relative humidity. We have further found that such sensors are stable in the presence of the gas, even at high concentration (e.g. 2000ppm), and do not age or become poisoned. Other sensors of the general  
20 formula  $\text{Cr}_{(2-x)}\text{Ti}_x\text{O}_3$ , where  $0.3 \geq x \geq 0.1$ , are by and large equally effective.

**Table 5: Sensor response to sulphur dioxide compared with response to change in relative humidity**

Composition:	$\text{Cr}_{1.8}\text{Ti}_{0.2}\text{O}_3$
Operating temperature:	500°C
5 Resistance in dry air:	10kohm
Resistance in wet air (100%RH at 20°C):	12 kohm
Resistance in dry air containing 400ppm $\text{SO}_2$ :	15 kohm

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**Sensors, and combinations of sensors, for various volatile organic compounds**

**(a) Chromium titanium oxide sensors**

Table 3, below, shows the response of sensors fabricated from  $\text{Cr}_{1.8}\text{Ti}_{0.2}\text{O}_3$  to a range of organic vapours, compared with the effect of a change in relative humidity from 0 to 100%. The effects of the organic vapours are large in comparison with the effects of water vapour, and in some cases are very large. The previous disclosures that are concerned with compositions including those in the range  $\text{Cr}_{(2-x)}\text{Ti}_x\text{O}_3$  implied that these compositions were insensitive to such vapours. The result exemplified in Table 3 is therefore surprising. We ascribe this result to differences in the detail of the preparation: in particular, we have found that a microstructure comprising very small crystallites ( $<1\mu\text{m}$  average diameter) with a very fine scale porosity (average pore diameter  $<1\mu\text{m}$ ) is necessary to confer such strong sensitivity.

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**Table 3: Response of sensors fabricated from  $\text{Cr}_{1.8}\text{Ti}_{0.2}\text{O}_3$  to a range of organic vapours, compared with the effect of a change in relative humidity from 0 to 100%**

5	gas	concentration /ppm	operating tempera- ture/°C	Resistance ratio: $R_{\text{gas}}/R_{\text{air}}$
10	water vapour	100%RH at 20°C	400	1.2 (compa- red with dry air)
	propane	1000	475	1.4
	butane	1000	475	1.4
	hexane	3000	475	2.7
15	hexane	3000	400	3.1
	petroleum (gasolene)	vapour above liquid at 20°C	475	5.6
	methanol	1000	460	3.1
	methanol	1000	250	>3.5
20	ethanol	1000	460	2.8
	ethanol	1000	250	>3.1
	propan-2-ol	200	400	8.4
	acetone	vapour above liquid at 20°C	500	9
25	butan-2-one	vapour above liquid at 20°C	475	6.3
	glutaraldehyde	1	400	1.2
	glutaraldehyde	3	400	1.5
	dimethoxyethane	5000	500	5.7

(b) Chromium iron niobate sensors

Table 4, below (and see also Figure 12), shows the response of sensors fabricated from  $\text{CrNbO}_4$  and  $\text{Fe}_{(1-x)}\text{Cr}_x\text{NbO}_4$  to a variety of organic vapours. The pattern of responses is different from that of  $\text{Cr}_{(2-x)}\text{Ti}_x\text{O}_3$ , and furthermore is also different from that shown by sensors made from  $\text{SnO}_2$ , or  $\text{SnO}_2$  doped with precious metals (Pt, Pd etc.), such as are common in the art. Therefore, combinations of such sensors can usefully be deployed in a sensor array, e.g. a so-called 'electronic nose', to discriminate between different vapours, using pattern-recognition methods, or principal component analysis, or standard methods of multivariate regression. The use of sensor materials such as those described here will confer advantage because such materials have such different patterns of response. Furthermore, the materials are much less sensitive to the effects of variable relative humidity, and are much more stable than those previously described: these attributes are particularly important in a sensor array system.

Figure 12 shows that a sensor made of  $\text{CrNbO}_4$  is particularly suitable for detection of CO. This is an important application of the invention.

**Table 4: Response of chromium iron niobates to various organic gases/vapours, compared with the effect of a change in relative humidity between zero and 100%**

5	sensor material	gas	concentration /ppm	operating temperature/°C	resistance $R_{gas}/R_{air}$
10	CrNbO <sub>4</sub>	water vapour	100%RH at 20°C	500	1.15 (compared with dry air)
15	CrNbO <sub>4</sub>	acetone	vapour over liquid at 20°C	500	13.8
	CrNbO <sub>4</sub>	dimethoxy-ethane	5000	500	4.0
	CrNbO <sub>4</sub>	hexane	3000	500	2.3
20	CrNbO <sub>4</sub>	petroleum	vapour over liquid at 20°C	500	9.0
25	*	methyl-methacrylate	20	500	0.73
	*	methyl-methacrylate	80	500	0.58
30	CrNbO <sub>4</sub>	CO (see Fig. 12)	400	400	1.94 (compared with dry air)
35	* Fe <sub>0.92</sub> Cr <sub>0.08</sub> NbO <sub>4</sub>				

**Sensor for carbon dioxide, at low concentration in air**

The document GB-A-2 149 121 discloses, as gas-sensitive resistors, compositions comprising a compound of tin of the general formula  $A_{(1-y)}B_ySn_{(1-x)}C_xO_{(3-z)}$ , where:

5 A is Ca, Sr or Ba; B is another alkaline earth element, another divalent element (e.g. Pb), or a trivalent lanthanide (e.g. La, Y, Gd); C is a tri- or tetra-valent element, for example a transition element (e.g. Fe, Co, Ti, Zr or Ce);  $1 > y \geq 0$ ;  $1 > x \geq 0$ ; and the oxygen  
10 deficiency, z, is determined by the atmosphere and cation composition of the solid.

In this range of materials,  $BaSnO_3$  is described in that document as having a response to  $CO_2$ . However, the  
15 response disclosed is to the presence of 100%  $CO_2$  in the atmosphere. Since it is also stated in that document that the composition showed a resistance change when the oxygen partial pressure changed, it is not clear whether  
20 a true response to  $CO_2$  had indeed been observed, rather than a response to the change in oxygen partial pressure caused when the air in the test chamber was replaced with carbon dioxide, carbon dioxide being well known to  
be chemically fairly inert.

Composites of  $BaSnO_3$  with  $CuO$  have recently been disclosed in the literature as being sensitive to  
25 relatively small concentrations of carbon dioxide in the air (typically 0.1%). It has been suggested that this effect is due to some special characteristic of the composite, involving some (unknown) interaction between  $CuO$  and  $BaSnO_3$ .



Along similar lines, claims have been made for carbon dioxide sensitivity of other CuO-containing composites, e.g. BaTiO<sub>3</sub> variously doped, e.g. with precious metals (e.g. in the document JP-A-05142180), leading to the inference that the characteristic is something to do with the presence of CuO, and that it involves some special synergistic interaction with the other component of the composite.

Surprisingly, we have now found that BaSnO<sub>3</sub> by itself exhibits a useful sensitivity to the presence of small concentrations of carbon dioxide in the air. We have further found that, although the presence of CuO serves to increase the speed of response somewhat, the main effect of CuO is to lower the electrical resistance of the composite into a range where measurements are more easily made. Even more surprisingly, and in direct contradiction to the presumptions arising from the earlier work cited above, we have found that the electrical resistivity of BaSnO<sub>3</sub> can be satisfactorily lowered by replacing a fraction of the Sn in the formula by a pentavalent element, particularly Sb,, and that sensors prepared from the resulting material show an electrical resistance varying by a useful amount in response to the presence of small additional concentrations of carbon dioxide in the air.

In an example, a material of composition BaSn<sub>0.99</sub>Sb<sub>0.01</sub>O<sub>3</sub> was prepared by conventional ceramic fabrication techniques, mixing powders of BaCO<sub>3</sub>, SnO<sub>2</sub> and Sb<sub>2</sub>O<sub>5</sub> in the appropriate proportions and firing in a furnace at 800°C. A sensor was prepared on a self-heated, planar substrate, as above, using conventional screen-printing fabrication methods. Figure 13 shows the variation in electrical resistance of this sensor

element in response to changes in the concentration of carbon dioxide in the air, being plotted over successive 5-minute periods, all at 350°C.

BaSnO<sub>3</sub> also, as disclosed in the document GB-A-2 149 121, shows resistance changes in response to the presence of small concentrations of reactive and flammable gases in the atmosphere. In order to distinguish such changes from those caused by variations in the concentration of carbon dioxide, a sensor comprising BaSn(1-x)Sb<sub>x</sub>O<sub>3</sub> (0 < x ≤ 0.1) as the sensitive element can be combined with another sensor which responds to the presence of reactive gases, but which does not respond to the presence of small concentrations of CO<sub>2</sub>. Suitable sensors include gas-sensitive resistors of composition Cr(2-x)Ti<sub>x</sub>O<sub>3</sub> or CrNbO<sub>4</sub> or Fe(1-x)Cr<sub>x</sub>NbO<sub>4</sub>, having the advantage of a relatively low response to the effect of changes in relative humidity, as discussed above; or SnO<sub>2</sub>, as is generally employed in the art. The interfering effect of changes in relative humidity on the sensor of composition BaSn(1-x)Sb<sub>x</sub>O<sub>3</sub> can be mitigated by using it in conjunction with a humidity sensor of conventional design, e.g. a capacitive device utilising aluminium oxide as the sensitive element.

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**Combinations of sensors useful for the monitoring of leaks of ammonia and chlorofluorocarbon refrigerants**

Tin dioxide is useful as a sensing element material in a gas-sensitive resistor responding to the presence of small concentrations in the air of chlorofluorocarbons (CFC) such as CF<sub>2</sub>Cl<sub>2</sub> (also known as R22). These agents are widely used as refrigerants but they have severe

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effects on the concentration of ozone in the upper atmosphere, so any leakage must be reliably and immediately detected. However, tin dioxide as a sensing element material suffers from the disadvantage of a strong effect of variations in relative humidity and also a strong response to many other reactive gases which might be present in the atmosphere, such as carbon monoxide emitted from internal combustion engines, or solvent vapours from cleaning agents, packaging and glue.

In particular, also,  $\text{SnO}_2$  shows a strong response to ammonia, which is also widely used as a refrigerant, and which may be used in conjunction with chlorofluorocarbons such as R22. In such cases, it is important to be able to distinguish a leakage of CFC from a leakage of ammonia. Sensors prepared with  $\text{Cr}_{(2-x)}\text{Ti}_x\text{O}_3$  as the gas-sensitive resistor element have, as noted above, a response to organic vapours, including carbon monoxide, and, as previously disclosed in GB-A-2 202 948, ammonia. However, they are relatively insensitive to variations of relative humidity (as disclosed above); importantly, they are also insensitive to the presence of a CFC (R22).

Therefore, a pair of sensors, one of which utilises  $\text{SnO}_2$  and the other  $\text{Cr}_{(2-x)}\text{Ti}_x\text{O}_3$ , will be able to distinguish a leak of CFC (signal only on  $\text{SnO}_2$ ) from one of ammonia (signal on both sensors), or a leak of CFC (signal only on  $\text{SnO}_2$ ), from the presence of solvent vapours or carbon monoxide (signal on both sensors).

A combination of these two sensors with a humidity sensor of conventional design, e.g. a capacitive device

utilising aluminium oxide as the sensitive element, will be able to discriminate all interferences. The humidity sensor, being unaffected by the refrigerant gases or by solvent vapours at environmentally significant concentrations, then provides a signal to compensate for the effect of relative humidity changes on the tin dioxide element, whilst the  $\text{Cr}_{(2-x)}\text{Ti}_x\text{O}_3$  provides a signal to compensate for the presence of solvent vapours.

Discrimination between the effects of ammonia and the effects of solvent vapours, and consequent avoidance of false alarms, can also be obtained by using a combination of a sensor fabricated from  $\text{Cr}_{(2-x)}\text{Ti}_x\text{O}_3$  with one fabricated from  $\text{Fe}_{(1-x)}\text{Cr}_x\text{NbO}_4$  ( $0 \leq x \leq 1$ ), or by using combinations of sensors fabricated from  $\text{Fe}_{(1-x)}\text{Cr}_x\text{NbO}_4$  with different values of  $x$ . For example, Table 6, below, shows a comparison of the response of these different materials to ammonia.

Comparison of the results in Table 6 with those in Tables 3 and 4 shows that  $\text{CrNbO}_4$  is much less sensitive to ammonia than  $\text{Cr}_{1.8}\text{Ti}_{0.2}\text{O}_3$ , but that it is equally, or more, sensitive to solvent vapours. A simple comparison of the signal from two such sensors would then give a false alarm due to the presence of solvent vapour.

However, in a sensor array comprising such a combination of sensors, if the signal from the  $\text{Cr}_{1.8}\text{Ti}_{0.2}\text{O}_3$  sensor is greater than that from the  $\text{CrNbO}_4$  sensor, then ammonia is present; if it is less, then solvent vapours are present. Tables 4 and 6 show that similar combinations of  $\text{Cr}_{1.8}\text{Ti}_{0.2}\text{O}_3$  with  $\text{Fe}_{(1-x)}\text{Cr}_x\text{NbO}_4$  ( $0 \leq x \leq 1$ ), or of sensors fabricated from

Fe<sub>(1-x)</sub>Cr<sub>x</sub>NbO<sub>4</sub> with different values of x, can be devised. Furthermore, a combination of any two of these sensors with a sensor fabricated from SnO<sub>2</sub> would, as described above, allow discrimination of solvent vapours, ammonia and CFC such as R22.

**Table 6: Comparison of response to 100ppm ammonia in air, of sensors fabricated from various materials**

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Sensor material	Operating temperature /°C	Resistance in 100ppm NH <sub>3</sub> in dry air/ Resistance in dry air
Cr <sub>1.8</sub> Ti <sub>0.2</sub> O <sub>3</sub>	430	1.77
CrNbO <sub>4</sub>	500	1.27
Fe <sub>0.92</sub> Cr <sub>0.08</sub> NbO <sub>4</sub>	500	0.53

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**20 Oxygen sensor material with small temperature dependence and insensitive to poisoning by sulphur dioxide**

Semiconducting oxide materials suitable for the measurement of changes in oxygen partial pressure, without interfering effects from the presence of hydrocarbons and carbon monoxide, are usually operated at rather high temperatures (greater than 500°C and up to 700°C). One problem is that sulphur dioxide is often present, sometimes at high concentration, in the gases to be measured, which might be, for example, the products of a combustion process which the oxygen sensor is deployed to control. Titanium dioxide has been used

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successfully for such applications. It is resistant to poisoning by sulphur dioxide, but has a high activation energy for electrical conductivity, leading to a temperature sensitivity of the conductance which is large in comparison with the effects of small changes in oxygen partial pressure, such as one might wish to measure to control a combustion system with excess oxygen (i.e. so-called lean mixture control). Materials such as the substituted barium ferrates, disclosed here and in US-A-4 454 494, have a very small activation energy, leading to a very small temperature sensitivity of the conductivity, and can be used to measure small changes in oxygen partial pressure. However, such materials degrade rapidly in the presence of SO<sub>2</sub>.

We have found that  $Ti(1-x)Cr_xO(2+y)$ , in which  $0.2 > x > 0$ , and y is variable according to the temperature and oxygen partial pressure, has an activation energy for conductivity which, whilst not as low as that of the barium ferrates, is half that of TiO<sub>2</sub>. Furthermore, the material has the same sensitivity to changes in oxygen partial pressure as does TiO<sub>2</sub>. Finally, the material is not degraded in the presence of sulphur dioxide at high concentration for extended periods of time (e.g. 2000ppm for some hours). Used as a sensor element deployed on a ceramic tile carrying a platinum heater track controlled in a Wheatstone bridge arrangement to operate at constant resistance and hence constant temperature, this material can be used to measure changes in oxygen partial pressure which are not as small as those detectable using substituted barium ferrates, but which are much smaller than those detectable using TiO<sub>2</sub> as the sensor element in a similar arrangement.

### Sensor for chlorine and nitrogen dioxide

Tungstic oxide ( $\text{WO}_3$ ) is well known as a sensor material when deployed in the form of a thin film; typically at most a few hundred nanometres thick. This material has  
5 been extensively studied as a sensor for hydrogen sulphide, and has been deployed commercially for this purpose. Such sensors have a reputation for poor calibration stability, and to be difficult to manufacture reproducibly. There has been mention in the  
10 literature of the sensitivity of these devices to the presence of hydrocarbons and carbon monoxide.

Now, surprisingly, we have found that this material, applied as a thick film, having a thickness typically of the order of some 100 micrometres but within a range of  
15 perhaps 10 - 200 micrometres, by screen printing onto a ceramic substrate carrying the electrodes for measurement of the resistance and having a printed heater on the reverse side, forms an excellent sensor for chlorine and nitrogen dioxide. The resistance  
20 changes in such a sensor, in the presence of low concentrations of these gases (of the order of 0.5ppm in air), are very large. The effect of hydrocarbons, solvents, ammonia and sulphur dioxide is small in comparison with the effect of chlorine and nitrogen  
25 dioxide. The sensor is not degraded by these gases. The baseline resistance and calibration are stable over time.

Figure 14 shows the resistance of such a  $\text{WO}_3$  sensor at 400°C to chlorine in three different concentrations  
30 (including zero) in air.

Figures 15 to 17 show the response of such  $\text{WO}_3$  sensors

to various concentrations of SO<sub>2</sub> at 400°C, CO at 500°C, and NO<sub>2</sub> at 500°C respectively. It can be seen that while the responses to SO<sub>2</sub> and CO at these temperatures are negligible, the sensor displays a strong response to both chlorine and NO<sub>2</sub>.

**Sensor for measurement of oxygen partial pressure, having a very low temperature dependence of conductivity**

Such a sensor in accordance with the invention, showing a change in its electrical resistance in response to changes in oxygen partial pressure, comprises at least one ferrate selected from SrFeO(3-x), BaFeO(3-x) and Sr(1-b)Ba<sub>b</sub>FeO(3-x), where x is a variable that determines the oxygen deficiency of the oxide. Its value depends on temperature as well as on the partial pressure of O<sub>2</sub>, but is typically in the inclusive range 0-0.5. b is in the inclusive range 0-1. In all cases, part of the iron in the ferrate lattice is replaced by at least one element having a valency of 6 or more, Zr being one example.

In an example, a powder mixture was prepared consisting of 1 mole of barium carbonate, 0.1 mole of tungsten oxide and 0.90 mole of calcined ferric oxide. The mixture was milled in the presence of acetone, using fine alumina media for four hours to obtain a very homogeneous mix. The resultant mixture was then dried in air to give a fine, homogeneously mixed powder, which was then ground. The powder was then made into a flexible tape by milling 30 grams of the powder with 60 grams of zirconia beads, 1.1 grams of dispersant, 25 ml. of trichlorethylene, milling overnight, adding 4.4 grams of binder and 1.1 grams of dibutylphthalate, milling



overnight for a second time, and casting under a doctor blade set at a thickness of 0.8 mm. After the tape had been dried, small pieces were cut from it, and moistened. These were placed onto interdigitated electrodes on alumina substrates, where they were fired according to a temperature regime designed to remove the organic material without disruption, and to cause the resulting mixed powders to react and to adhere firmly.

The resultant sensor was heated with a platinum resistance element printed on to the reverse side of the alumina tile and maintained at a temperature of 750°C. The sensor thus produced then afforded responses to changes in oxygen partial pressure as shown in Figures 18 and 19. These results are reproducible over several cycles and, when interrogated with a conventional DC measurement system, they show none of the response distortion which is exhibited by compositions quoted in the document US-A-4 454 494 when interrogated by DC resistance measurement systems.

The new composition is of significant advantage for the accurate measurement of oxygen without recourse to AC measurement systems.

#### **Sensor configurations with reference to the electrical interrogation of the gas sensitive materials**

Figure 20 shows, purely diagrammatically, the conventional configuration of a semiconductor gas sensor, whereby the latter has four wires for electrical connection. Two of these, 10 and 11, are attached to a pair of electrodes 12 and 13, which are bridged by the gas sensing element 14, the resistance of which is to be

measured. The other two wires 15 and 16 supply a resistance heating element 17, which is typically electrically insulated from the sensing element 14, for example by a layer of alumina 18 with the heating  
5 element 17 on one side and the sensing element 14 on the other.

When sensor element materials are used that have a resistance within a suitable range of values, however, it is possible to use fewer wires, with the advantage  
10 that heat loss by conduction is reduced. The sensor can then achieve its operating temperature with reduced power input.

For example, when the resistance of the sensing material during operation remains high with respect to the  
15 resistance of the heating element, then it is possible for the sensing part and heating part to have one wire 20 in common, thus reducing the number of wires to three as seen in Figure 21.

Again, when the resistance of the sensing element  
20 material at the operating temperature is of similar magnitude to that of the heating element, it is possible to have the sensing element in contact with the heater, as a parallel resistor, i.e. omitting the layer 18. Gas sensing will then be achieved by measuring the combined  
25 resistance, through two wires only.

These alternative interrogation configurations can be applied, with advantage, to any sensor made with the materials disclosed herein.

## CLAIMS

1. A gas sensor comprising a semiconducting sensing element such that its electrical resistance changes in response to a change in the concentration of at least one gas or vapour, constituting a target gas, that is present, to a greater extent than to other gases or vapours, whereby the sensing element is selective in favour of the target gas, so as to detect the latter, characterised in that the sensing element is of a material selected from the following materials:
- (i)  $\text{Ba}_6\text{Fe}_{(1+x)}\text{Nb}_{(9-x)}\text{O}_{30}$ , where  $2.1 > x \geq 0$ ;
  - (ii)  $\text{A}_2\text{B}_4\text{Fe}_{(3+x)}\text{Nb}_{(7-x)}\text{O}_{30}$ , where A is a divalent element of large ionic size, B is a trivalent element, and  $3.1 \geq x \geq 0$ ;
  - (iii)  $\text{A}_6\text{B}_4\text{Fe}_{(4+x)}\text{Nb}_{(6-x)}\text{O}_{30}$ , where A is a trivalent element of large ionic size, B is a trivalent element, and  $4.1 \geq x \geq 0$ ;
  - (iv)  $\text{Cr}_{(2-x)}\text{Ti}_x\text{O}_3$ , where  $0.3 \geq x \geq 0.1$ ;
  - (v)  $\text{Ti}_{(1-x)}\text{Cr}_x\text{O}_{(2+y)}$ , where  $0.2 \geq x \geq 0$ , and y is a variable dependent on temperature and on partial pressure of oxygen;
  - (vi)  $\text{Fe}_{(1+x-z)}\text{A}_2\text{Nb}_{(1-x)}\text{O}_4$ , where  $0.1 \geq x \geq 0$ ,  $0.1 \geq z \geq 0$ , and A is selected from the pentavalent and hexavalent metals;
  - (vii)  $\text{Fe}_{(1-x)}\text{B}_x\text{NbO}_4$ , where B is selected from:
    - trivalent elements, with  $1 \geq x \geq 0$ , and
    - tetravalent elements, with  $0.1 \geq x \geq 0$ ;

(viii)  $(\text{Fe}_{(1-x)}\text{Cr}_x\text{NbO}_4)_a(\text{B}_{(1-y)}\text{A}_y\text{O}_2)_{(1-a)}$ , where  $1 \geq a \geq 0$ ,  $1 \geq x \geq 0.1$ ,  $0.1 \geq y \geq 0$ , A is an element of valency greater than 4, and B is Ti or Sn;

(ix)  $\text{BaSn}_{(1-x)}\text{Sb}_x\text{O}_3$ , where  $0 \leq x < 0.1$ ;

5 (x)  $\text{Sr}_{(1-b)}\text{Ba}_b\text{Fe}_{(1-y)}\text{A}_y\text{O}_{(3-x)}$ , where  $1 \geq b \geq 0$ ,  $0.5 \geq x \geq 0$ , A is an element of valency greater than 5, and y is a fraction of the ferrate lattice replaced by A; and

(xi)  $\text{WO}_3$ ,

10 and in that the material is selected as follows in accordance with the following target gases to be detected:

- hydrocarbons other than methane (in the presence of CO): any of (i) to (iii);
- hydrocarbons other than methane (whether or not CO is present): any of (i) to (iv);
- 15 - methane: any of (i) to (iii);
- aldehydes, ketones, ethers, diethers: (iv); (vi); (vii); (viii);
- esters, including unsaturated esters: (vi);
- 20 (vii); (viii);
- chlorine or  $\text{NO}_2$ : (vi); (vii); (xi);
- any oxidising gas (especially in the presence of hydrocarbons and/or CO): (vi); (vii);
- $\text{H}_2\text{S}$ ,  $\text{SO}_2$ : (iv);
- 25 - CO: (iv); (viii);

- CO<sub>2</sub>: (ix); (iv); (viii);
- chlorofluorocarbons (CFC): (iv); (viii);
- ammonia: (iv); (vii);
- free oxygen: (v); (x).

- 5     2. A sensor according to Claim 1 in which the sensing element is of material (i), characterised in that  $0.8 > x \geq 0.01$ .
3. A sensor according to Claim 2, characterised in that x is 0.4 or 0.6.
- 10    4. A sensor according to Claim 1 in which the sensing element is of material (ii), characterised in that A is Pb, and/or B is Nd.
5. A sensor according to Claim 1 in which the sensing element is of material (iii), characterised in that A is Bi, and/or B is selected from Nd and Bi.
- 15    6. A sensor according to Claim 1 in which the sensing element is of material (iv), characterised in that the sensing element has a microstructure in which the average crystallite diameter and average pore diameter
- 20    are both smaller than 1 micrometre.
7. A sensor according to Claim 1 in which the sensing element is of material (vi), characterised in that the pentavalent element is selected from Nb and Ta, and/or the hexavalent element is W.
- 25    8. A sensor according to Claim 1 in which the sensing element is of material (vii) with B trivalent, characterised in that B is selected from Al and Cr.

9. A sensor according to Claim 1 in which the sensing element is of material (vii) with B tetravalent, characterised in that B is selected from Zr and Ti.

10. A sensor according to Claim 1 in which the sensing element is of material (viii), characterised in that A is selected from Nb, Ta, W and Sb.

11. A sensor according to Claim 1 in which the sensing element is of material (viii), characterised in that the said material is selected from  $\text{CrNbO}_4$  and  $\text{Fe}_{(1-x)}\text{Cr}_x\text{NbO}_4$ , where  $1 > x > 0.1$ .

12. A sensor according to Claim 1 in which the sensing element is of material (x), characterised in that A is selected from W, Mo and U.

13. A sensor according to Claim 1 having a  $\text{WO}_3$  sensing element, characterised in that the sensing element is in the form of a film, with the sensor including a heating element for heating the film so that the latter, when heated, displays in response to the presence of 0.5 parts per million of chlorine or  $\text{NO}_2$  in air a resistance substantially higher than in response to  $\text{SO}_2$  or  $\text{CO}_2$ .

14. A sensor according to Claim 13, characterised in that the thickness of said film is in the inclusive range 10 - 200 micrometres.

15. A sensor according to Claim 14, characterised in that the said thickness is 100 micrometres.

16. A sensor according to any one of the preceding Claims, including a heating element (17) for heating the sensing element (14), and electrical connecting means connected variously to the sensing element and heating

element, characterised in that said connecting means comprise first connection means (10, 15) connected to the sensing element, and a common electrical connection (20) connected to both of said elements (14, 17).

5 17. A sensor according to Claim 16, characterised in that one of the said elements (14, 17) is overlaid on the other so that they work as two resistors in parallel, the said first connection means comprising a further connection common to both of said elements (14,  
10 17).

18. A sensor array for detecting at least one gas or vapour constituting a target gas, characterised in that the array comprises at least one first sensor, being a sensor according to any one of the preceding Claims, in  
15 combination with at least one further sensor having a characteristic response, to at least one said target gas and/or at least one further gas or vapour that may be present, different from that of said first sensor.

19. An array according to Claim 18, characterised in  
20 that said first sensor is a sensor according to Claim 1 in which the sensing element is of material (vii) with B being trivalent and  $1 \geq x \geq 0$ , a said further sensor being a sensor according to Claim 1 having its sensing element material selected from material (iv) and material (vii),  
25 with, in the latter case B trivalent and x having a different value from that in the material of said first sensor, for detection of chlorofluorocarbon in the presence of ammonia and/or organic vapour.

20. An array according to Claim 19, characterised in  
30 that said first sensor is of  $\text{CrNbO}_4$ .

21. An array according to Claim 18, in which said first sensor is a sensor according to Claim 1 in which the sensing element is of material (iv), or according to Claim 19 or Claim 20, characterised in that,  
5 respectively, the said further sensor or another said further sensor has a sensing element of SnO<sub>2</sub>.

22. An array according to Claim 18, characterised in that said first sensor is a sensor according to Claim 11, for detection of organic vapours.

10 23. An array according to Claim 18, characterised in that said first sensor is a sensor according to Claim 1 in which the sensing element is of material (ix), at least one second sensor being a sensor responsive to reactive and/or flammable gases but substantially non-  
15 responsive to CO<sub>2</sub> at low concentrations to which said first sensor shows a significant response.

24. An array according to Claim 23, characterised in that the said second sensor is a sensor according to Claim 1 in which the sensing element is of material (iv) or material (viii), for detection of low CO<sub>2</sub>  
20 concentrations.

25. An array according to Claim 24, characterised in that the or a said second sensor is a sensor according to Claim 11.

25 26. An array according to any one of Claims 23 to 25, characterised in that it further includes a humidity sensor arranged for mitigating effects of relative humidity on said first sensor.

27. A method of making an element for a sensor  
30 according to any one of Claims 1 to 17, characterised by



the step of adjusting the sintering temperature to control the microstructure, and therefore the selectivity, of the sensing element.

5 28. A method of making a sensor element according to Claim 1 of material (iv), characterised by the pretreatment of the sensor element material by exposure to an atmosphere containing  $H_2S$ , so as to increase the amplitude and speed of the response of the sensor element to the presence of  $H_2S$ .

10 29. A method according to Claim 28, characterised in that the pretreatment step comprises exposing the material to  $H_2S$  in a concentration of 10 parts per million for between 1 and 10 minutes at a temperature greater than  $200^{\circ}C$  and less than  $600^{\circ}C$ .

15 30. A method of detecting at least one gas or vapour, constituting a target gas, characterised by the use of at least one sensor according to any of Claims 1 to 17, or an array according to any of Claims 18 to 22, to produce an electrical resistance signal representing the  
20 amount of target gas or gases present.

31. A method according to Claim 30 for measuring hydrocarbons in motor vehicle exhaust gas, characterised by the use of at least one sensor according to Claim 1 in which the sensing element is of a material selected  
25 from materials (i) to (iii), or according to any one of Claims 2 to 5.

32. A method according to Claim 30 using a sensor according to Claim 1 or Claim 6, the sensor element being of material (iv), characterised in that the sensor  
30 detects  $H_2S$  in an aerobic or anaerobic atmosphere, or

organic vapours, or SO<sub>2</sub>, or CO, or hydrocarbons other than methane in the presence of methane and/or hydrogen.

33. A method according to Claim 32 when used for the detection of CO leakage from a gas-fired appliance.

5 34. A method according to Claim 30 using a sensor according to Claim 11 for detection of organic vapours.

35. A method according to Claim 34 when used for detecting CO.

10 36. A method according to Claim 30 for measurement of oxygen partial pressure, characterised by the use of a sensor according to Claim 1 in which the sensing element is of material (v), or of material (x), the method including applying heating to maintain the sensor at a constant temperature.

15 37. A method according to Claim 30 for detecting the presence of chlorofluorocarbon, characterised by the use of an array according to Claim 19 or Claim 20.

20 38. A method according to Claim 37, characterised in that the array is an array according to Claim 21, so as, in addition, to detect the presence of ammonia and/or solvent vapour.

25 39. A method according to Claim 30 for monitoring small concentrations of CO<sub>2</sub> in at least partly closed-circuit atmospheres, characterised by the use of an array according to any one of Claims 23 to 26.

1/13

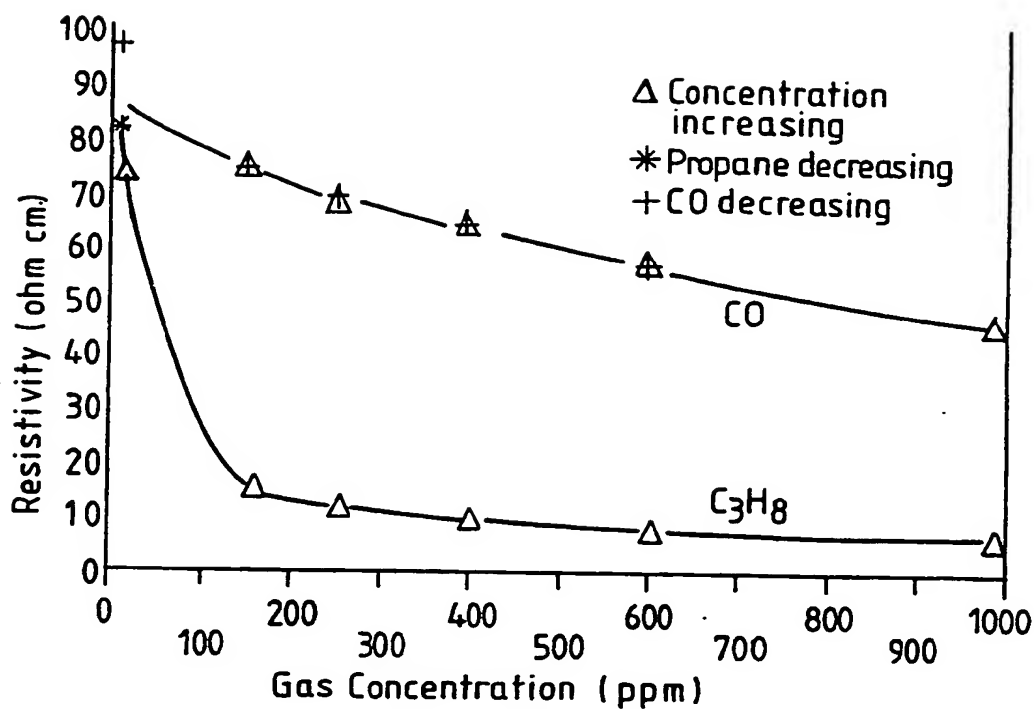


Fig.1.

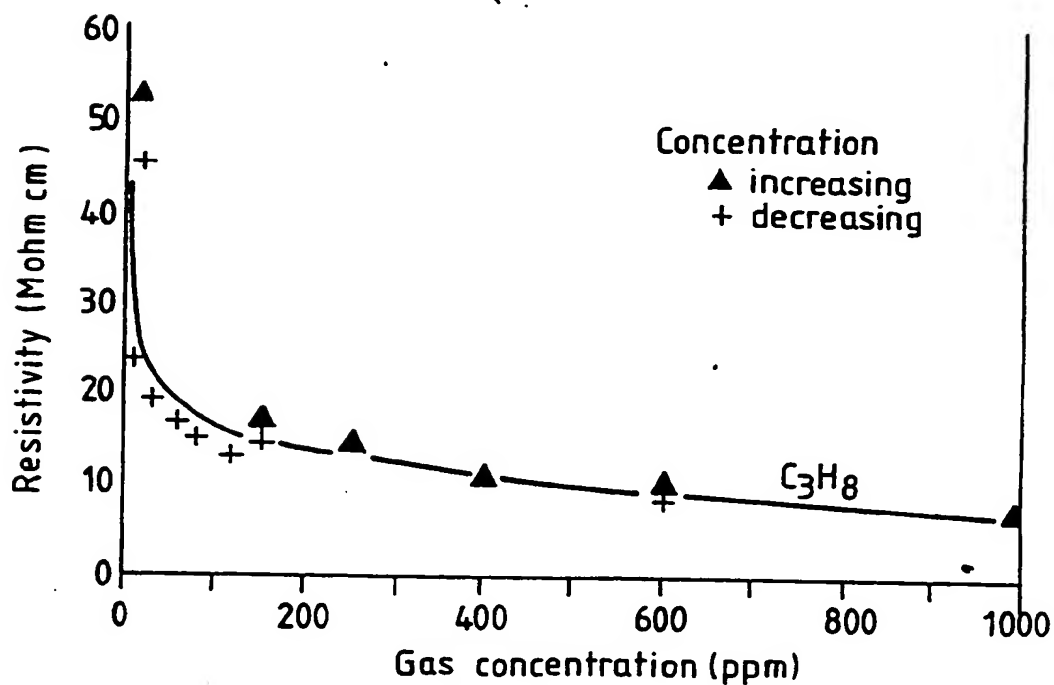


Fig.2.

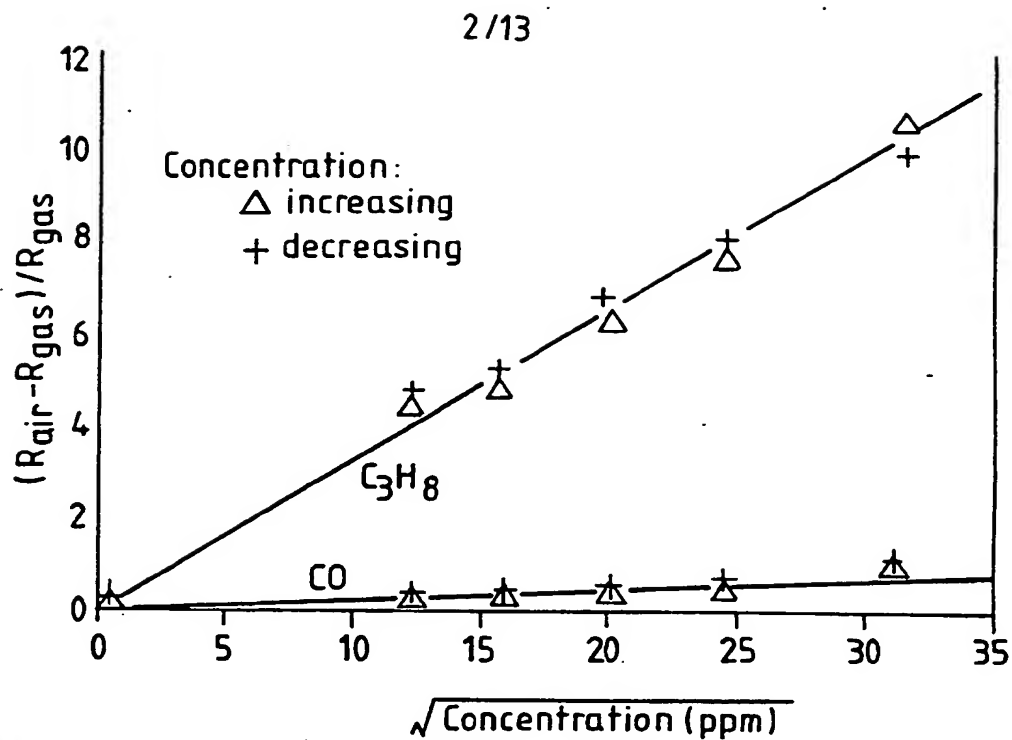


Fig.3.

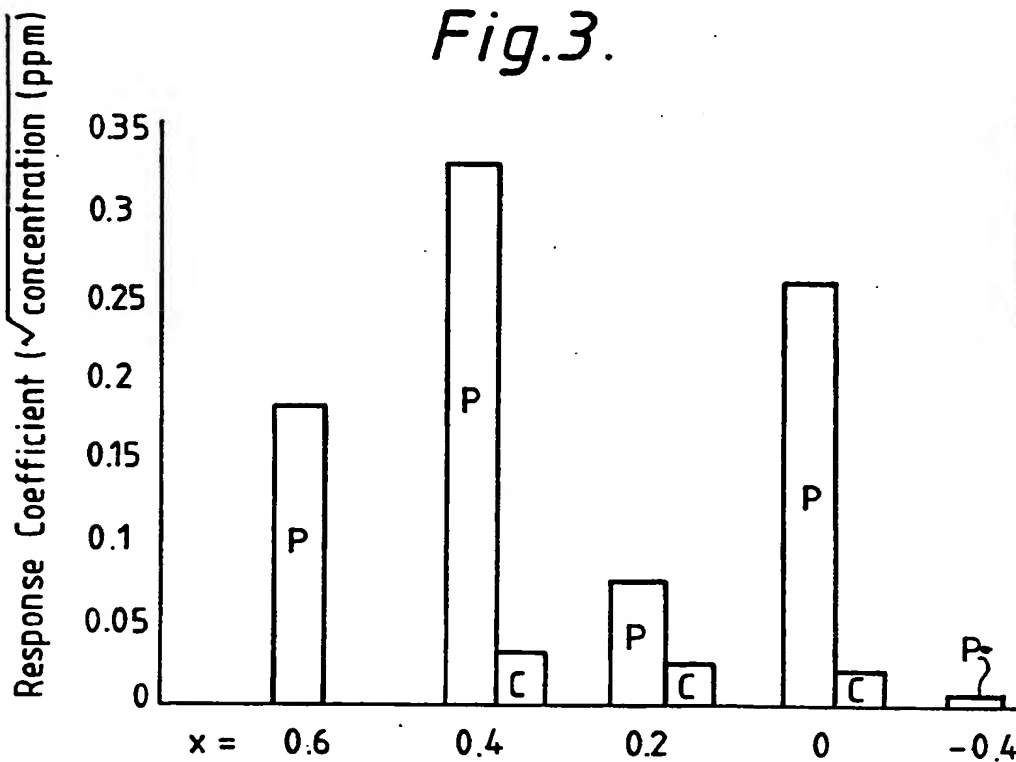


Fig.4.

3/13

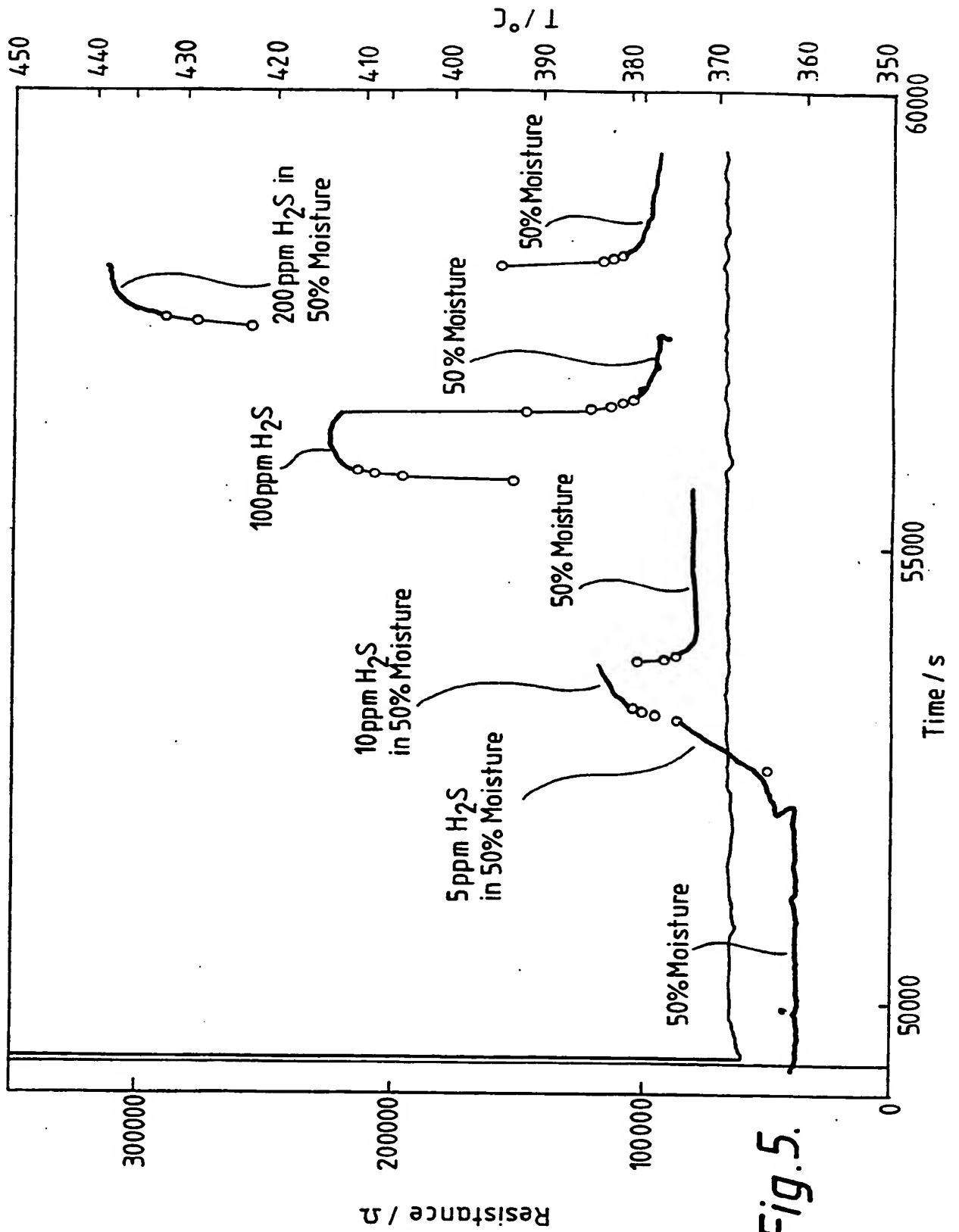


Fig. 5.

4/13

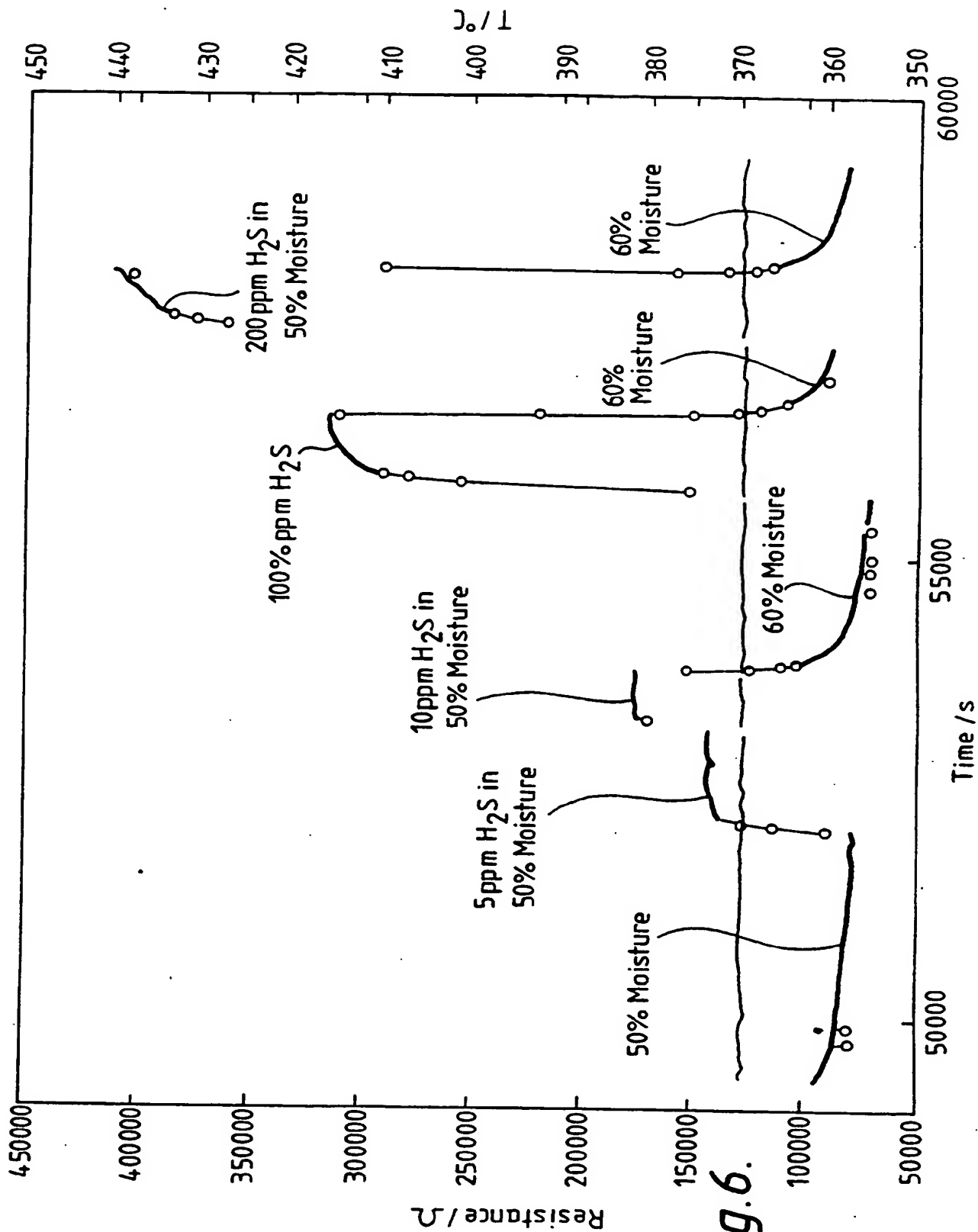
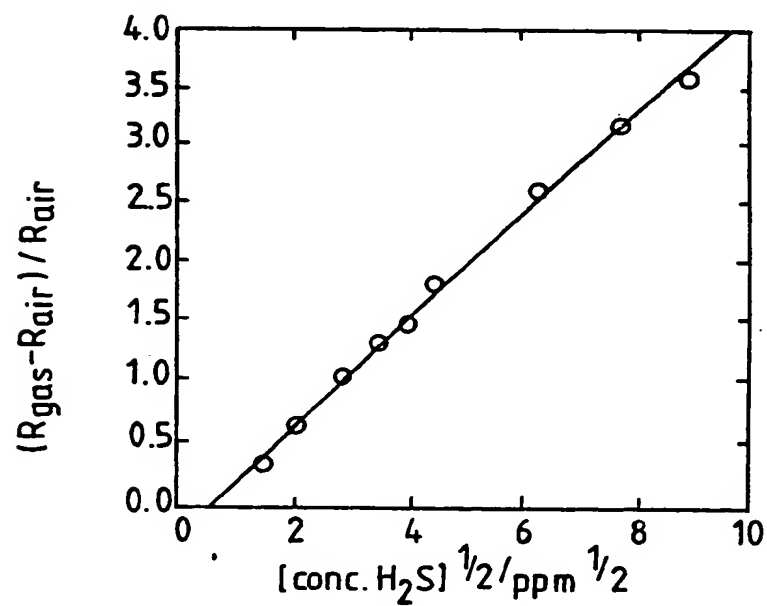
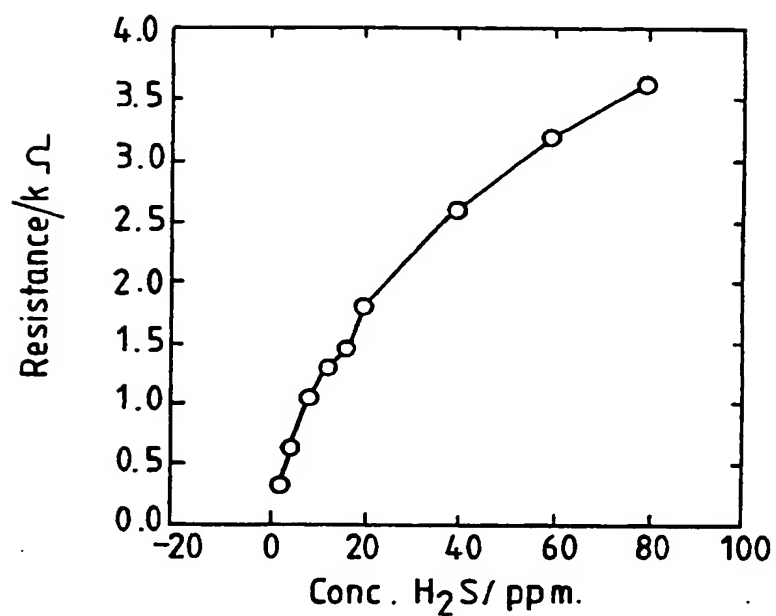
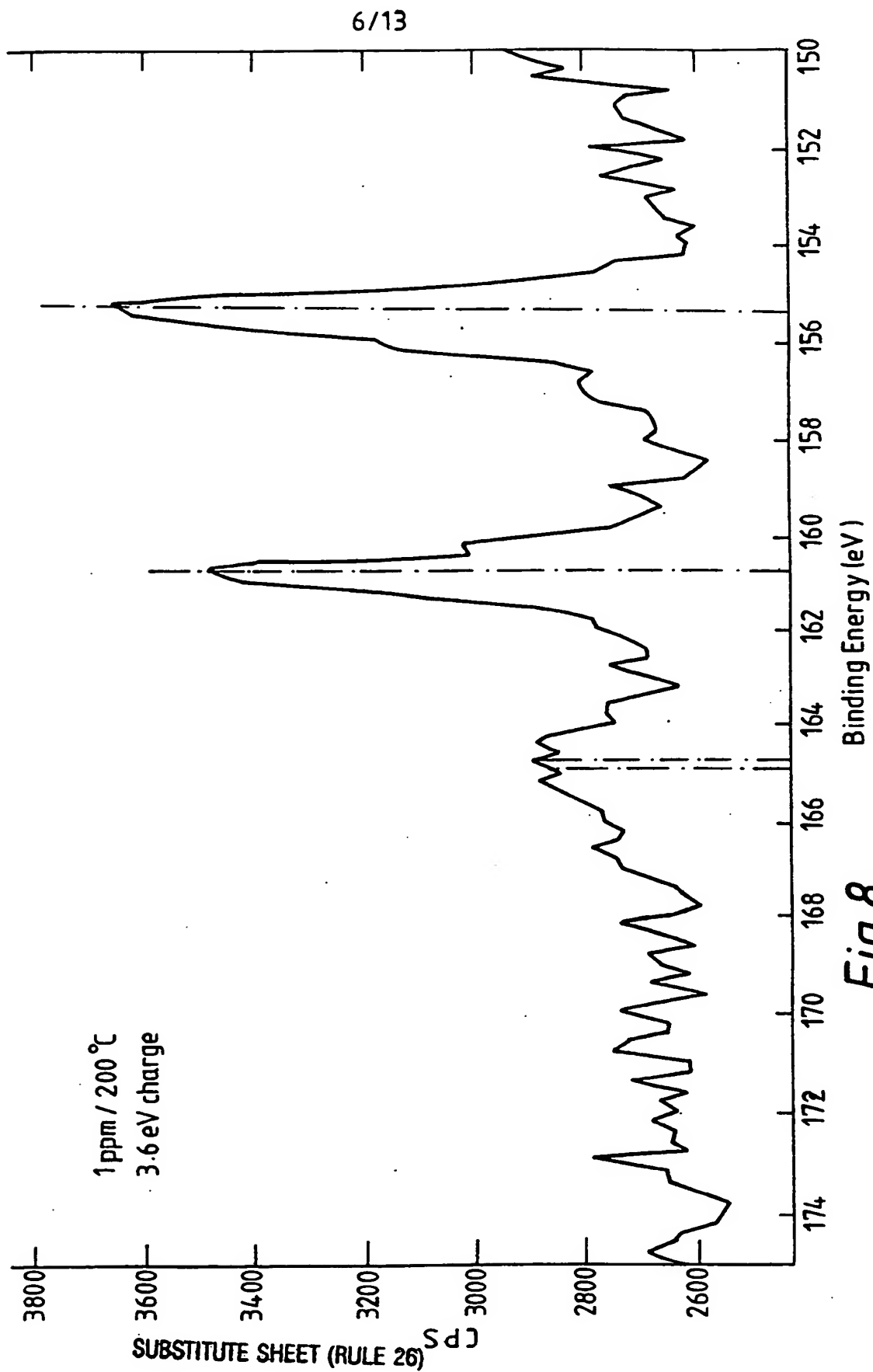


Fig. 6.

5/13

CrTiO (Reacted) Device Sintered  
at 800 °C.

*Fig. 7.*





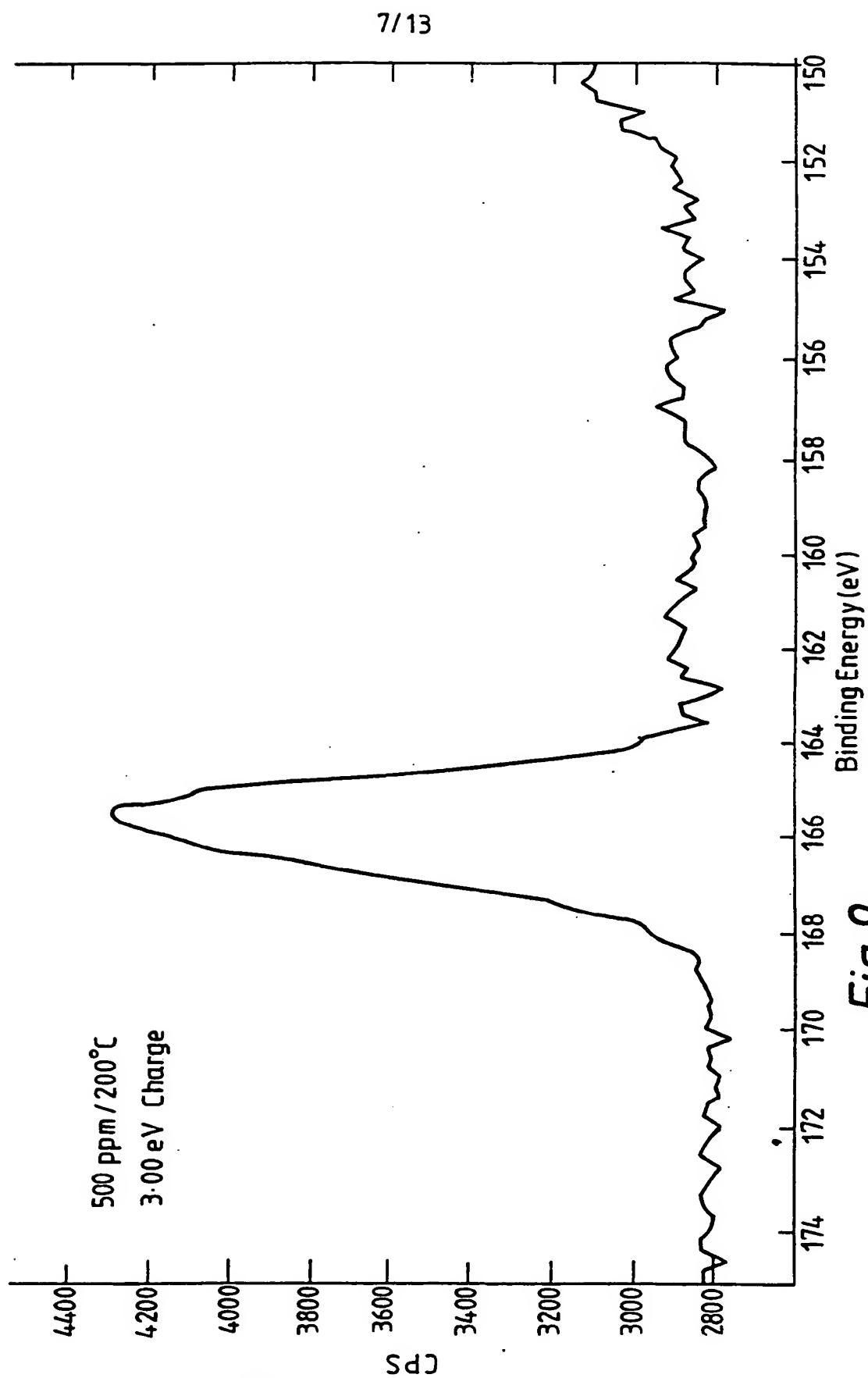


Fig. 9.

8/13

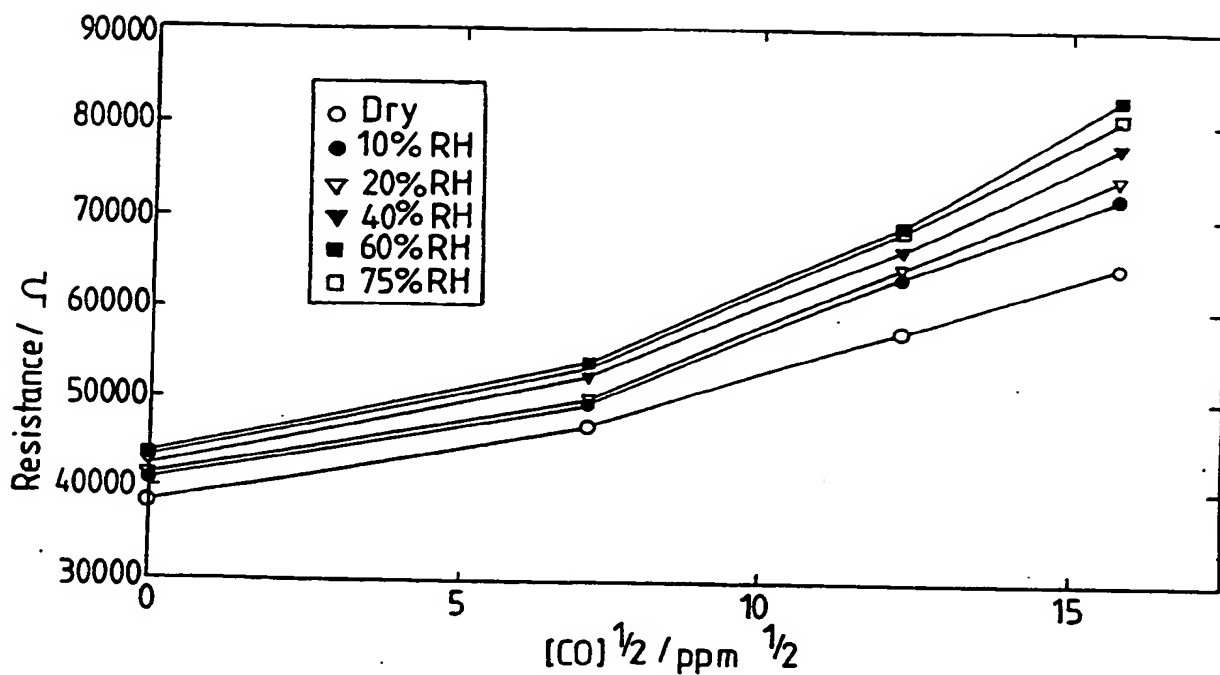


Fig.10.

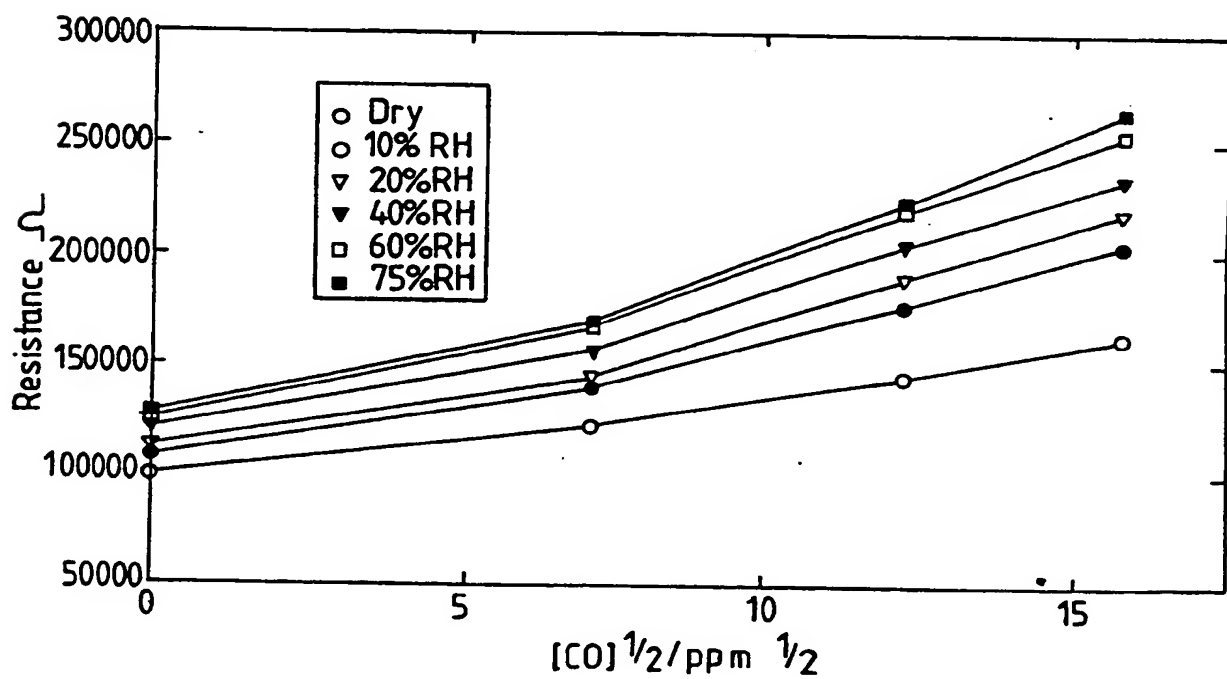


Fig.11.

9/13

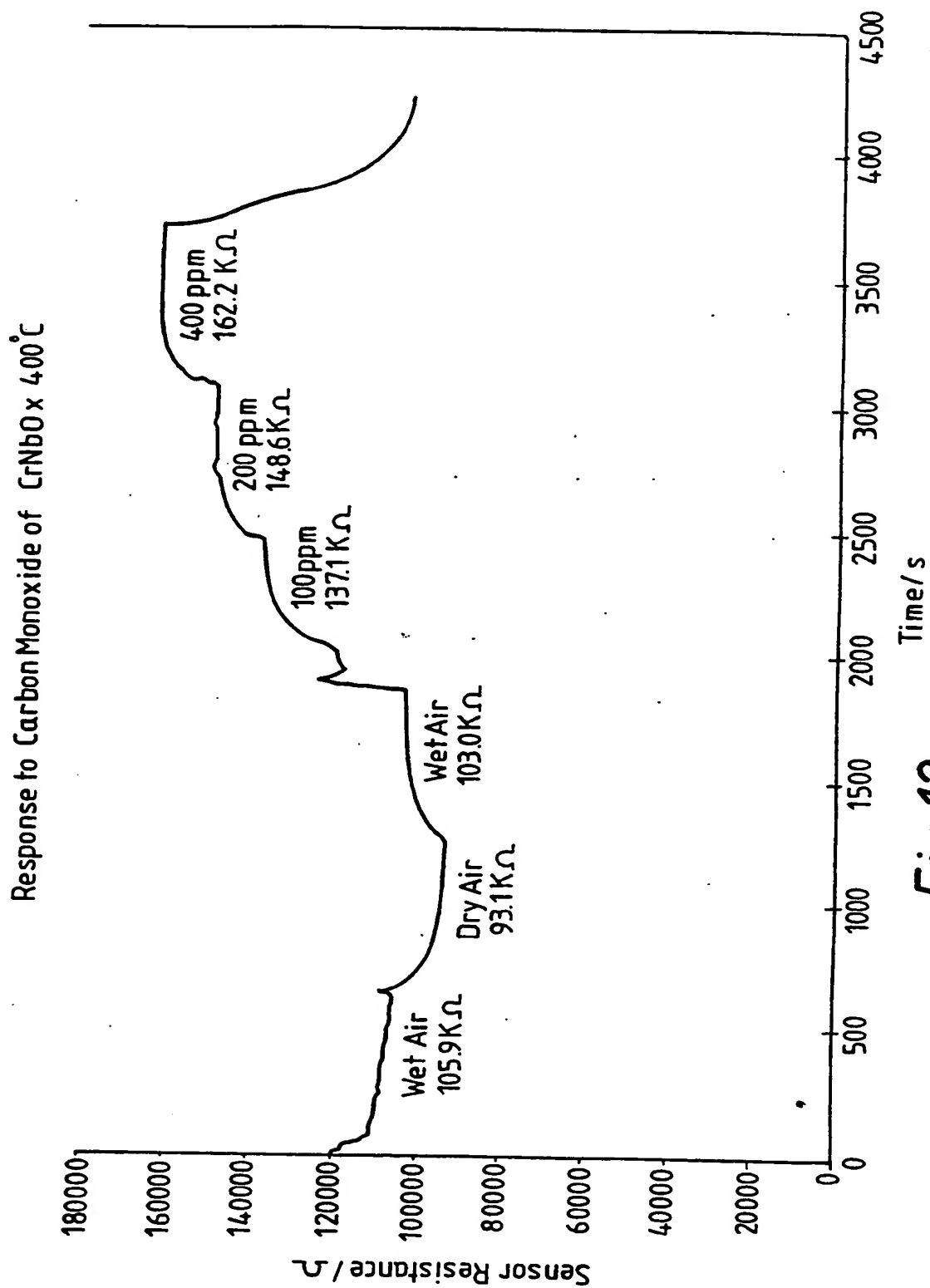
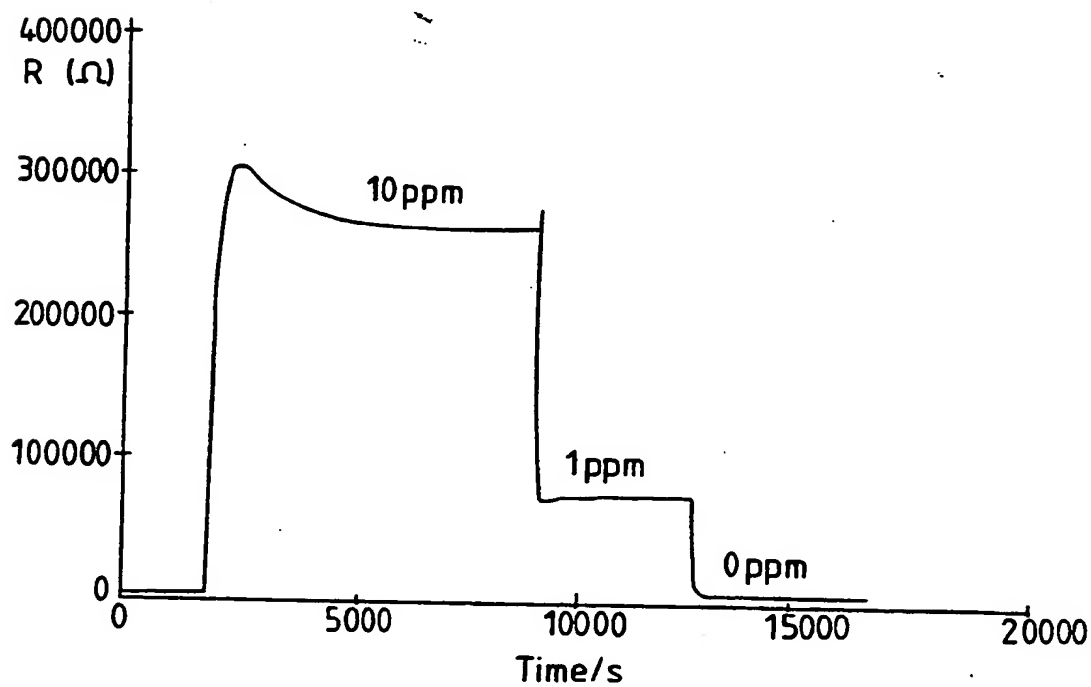
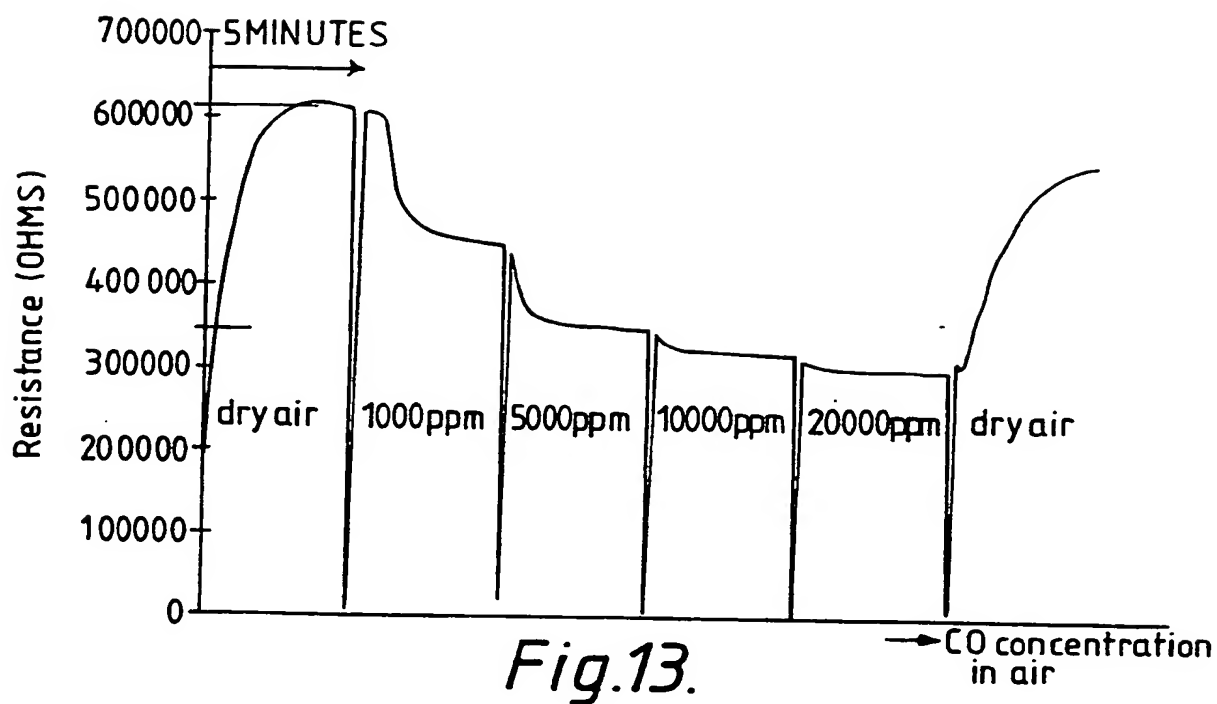


Fig.12.

10/13



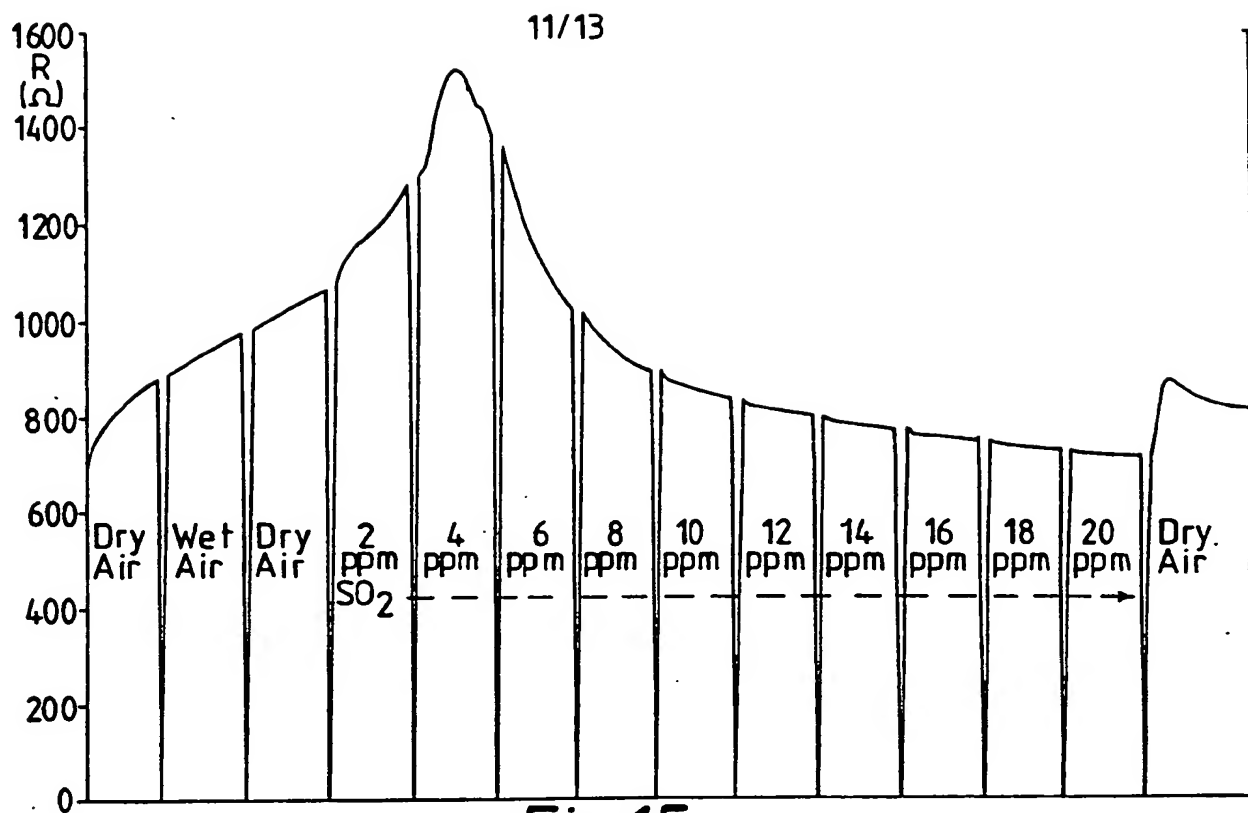


Fig.15.

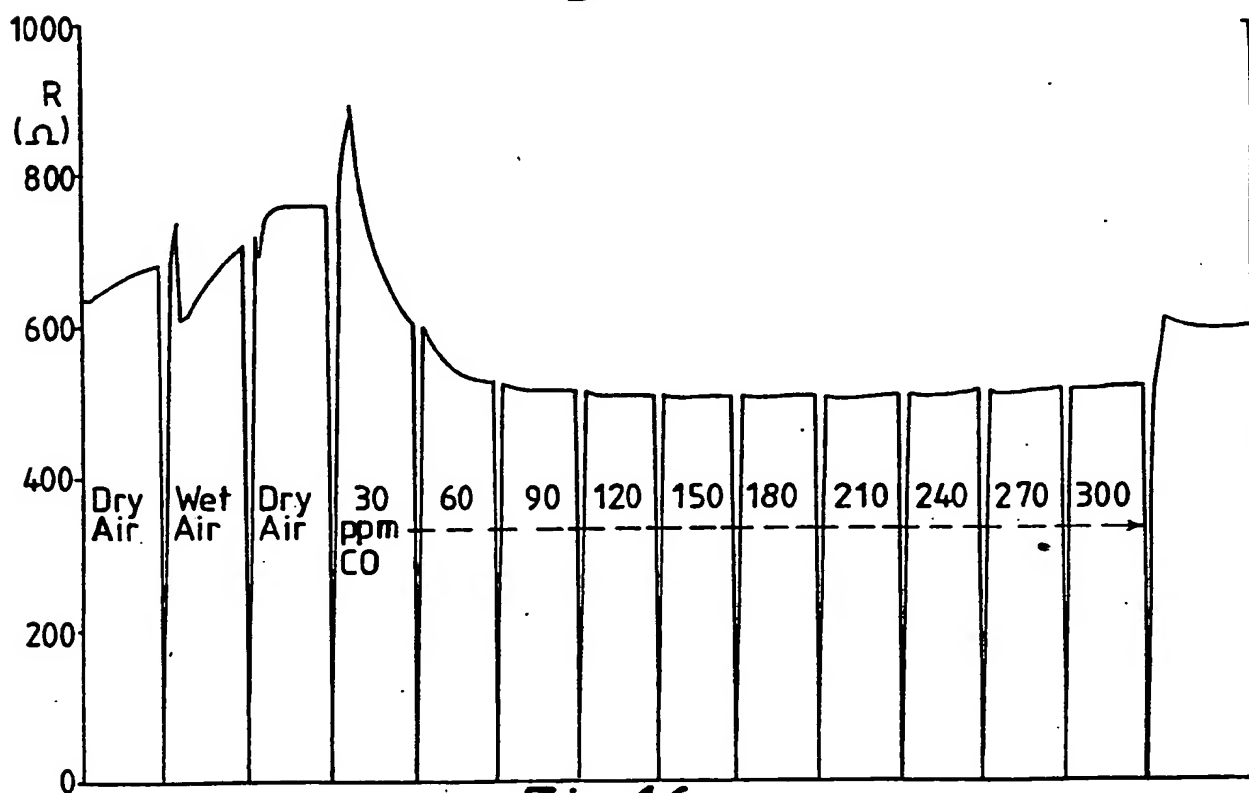


Fig.16.

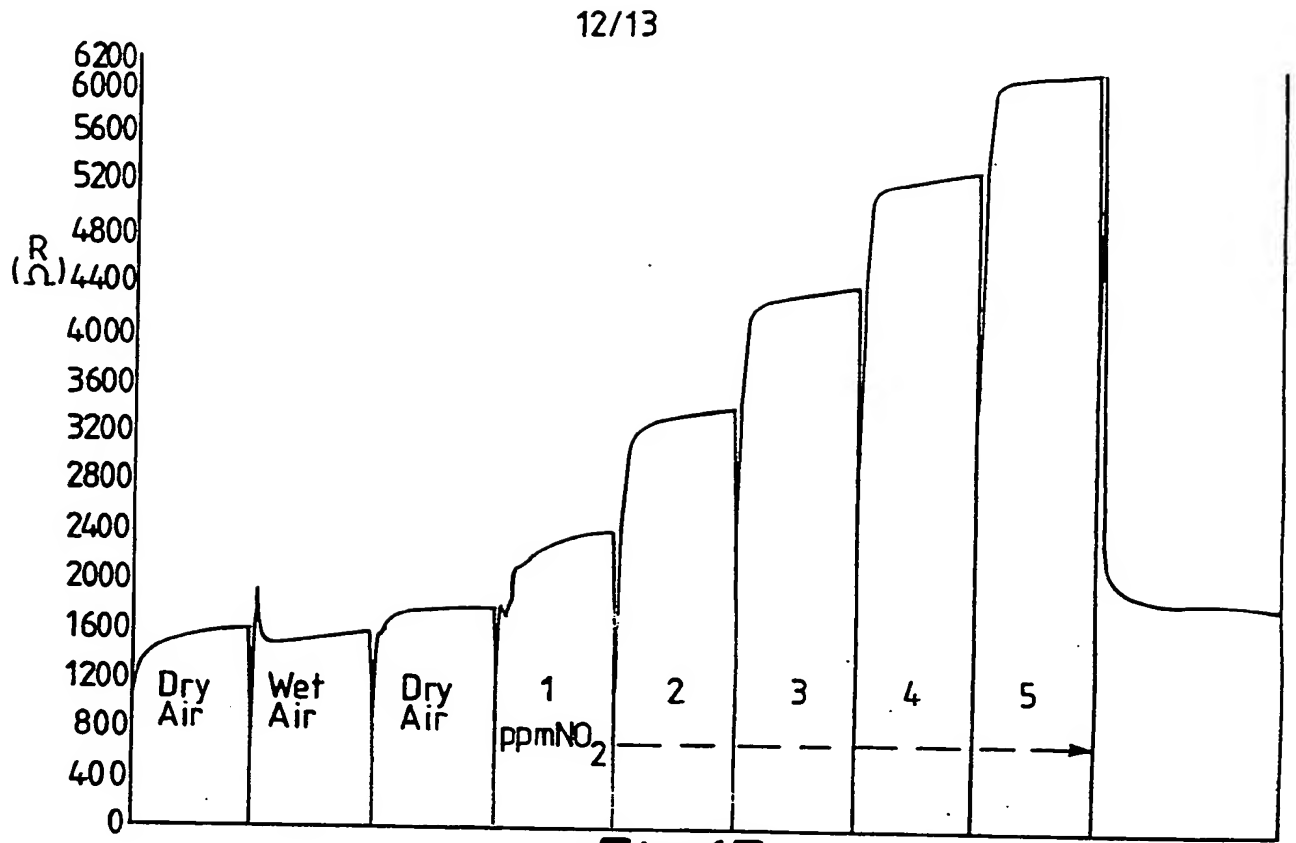


Fig.17.

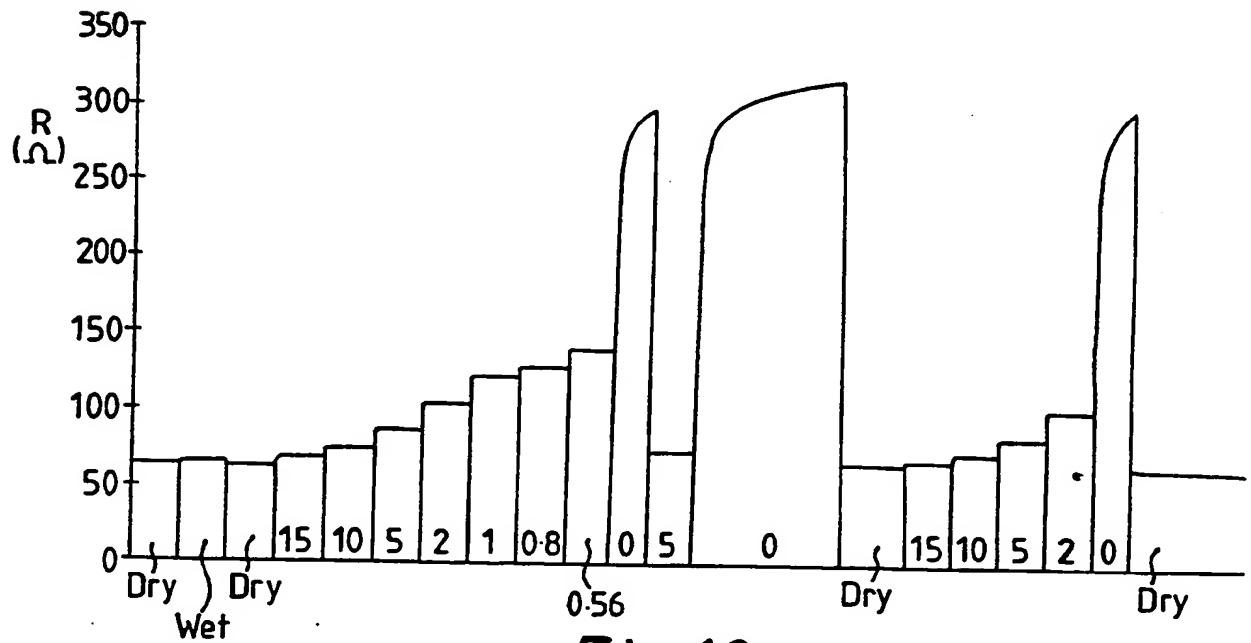
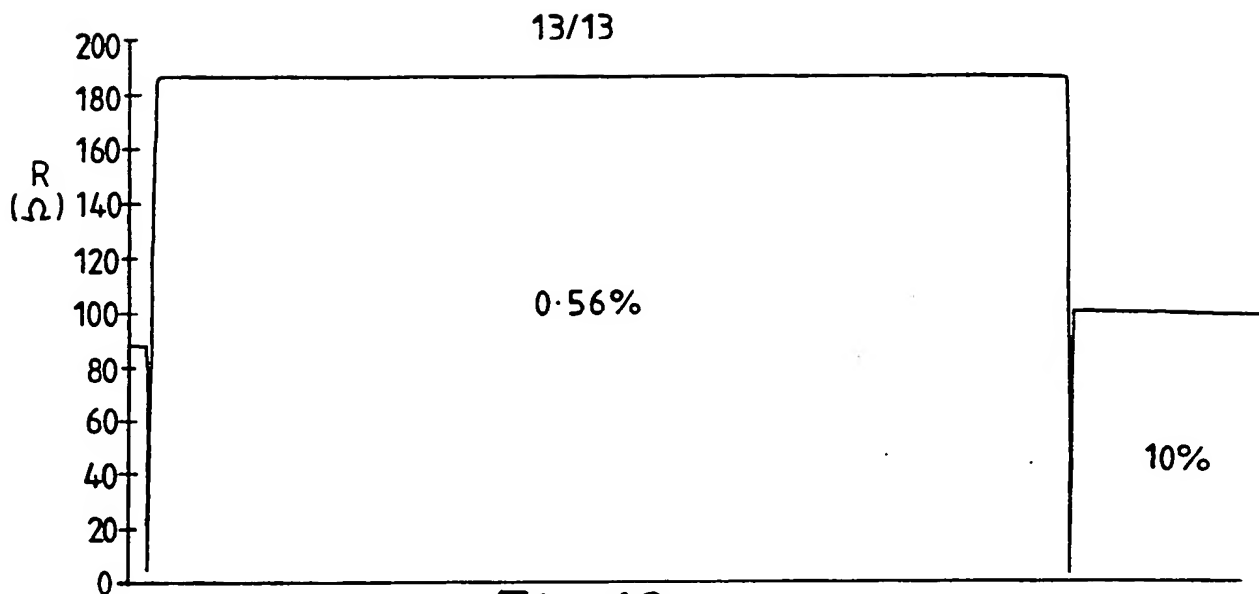
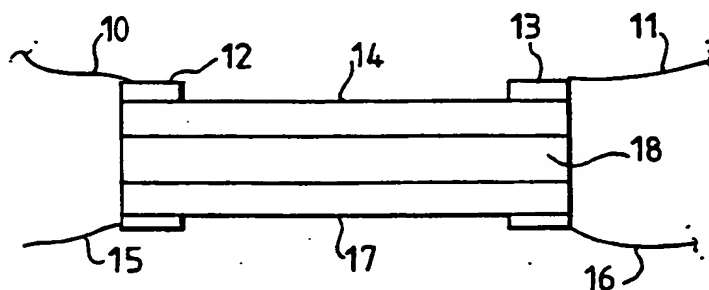


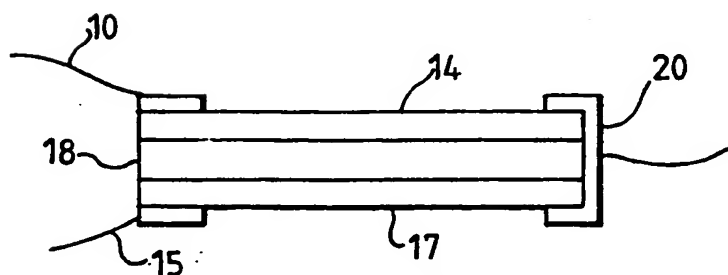
Fig.18.



*Fig.19.*



*Fig.20.*



*Fig.21.*

## INTERNATIONAL SEARCH REPORT

Int. onal Application No

PCT/GB 94/01327

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 G01N27/12

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB,A,2 149 122 (UNITED KINGDOM ATOMIC ENERGY AUTHORITY) 5 June 1985	1-4
Y	see abstract; claim 19; figure 1; table 1	18
Y	DE,A,32 13 286 (HITACHI LTD) 20 October 1983	18
	see abstract; claim 1; figure 4	
A	US,A,4 007 435 (TIEN) 8 February 1977	1,31
	see abstract; figures 1,3	
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

23 September 1994

Date of mailing of the international search report

17. 10. 94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+ 31-70) 340-3016

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Kempf, G



## INTERNATIONAL SEARCH REPORT

Int. Patent Application No  
PCT/GB 94/01327

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JOURNAL OF MATERIALS CHEMISTRY, vol.1, no.5, 1991 pages 809 - 814 DAVID E. WILLIAMS AND PATRICK T. MOSELEY 'Dopant Effects on the Response of Gas-sensitive Resistors Utilising Semiconductor Oxides' cited in the application see the whole document -----	1

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. Appl. No.

PCT/GB 94/01327

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A-2149122	05-06-85	NONE	
DE-A-3213286	20-10-83	NONE	
US-A-4007435	08-02-77	NONE	